Macmillan

UNIVERSITY GENERAL CHEMISTRY

An Introduction to Chemical Science

Edited by
CNR RAO

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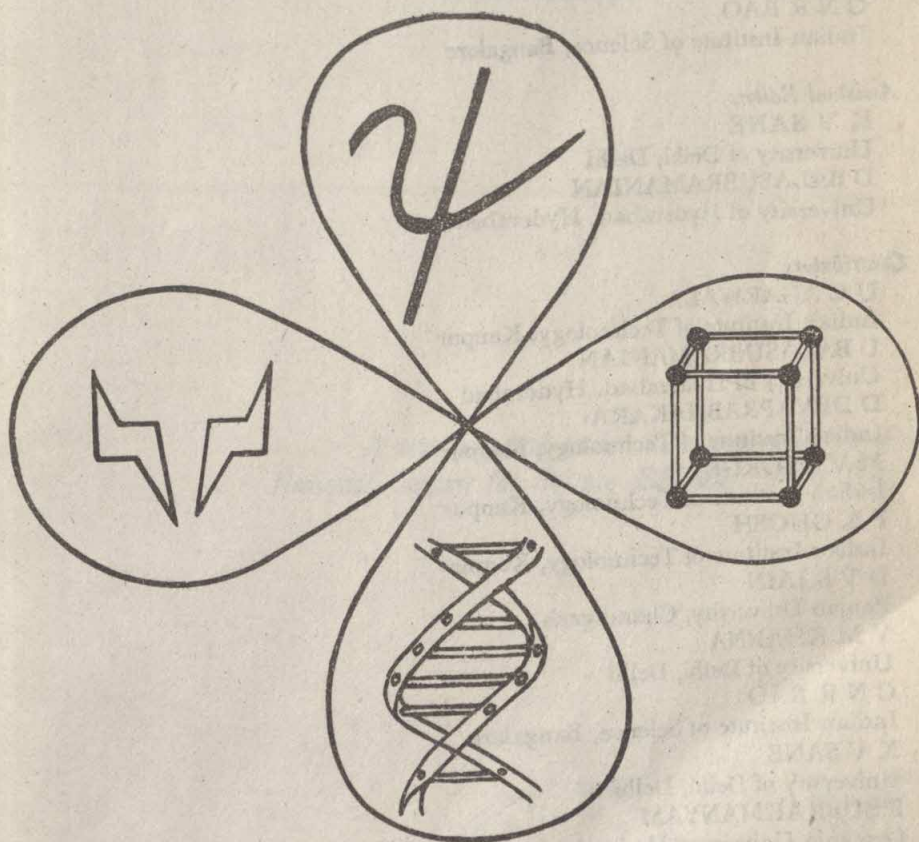| Element*	Atomic Number	Atomic Mass†	Element	Atomic Number	Atomic Mass
Actinium (Ac)	89	(227)	Erbium (Er)	68	167·26
Aluminum (Al)	13	26·9815	Europium (Eu)	63	151·96
Americium (Am)	95	(243)	Fermium (Fm)	100	(253)
Antimony (Sb)	51	121·75	Fluorine (F)	9	18·9984
Argon (Ar)	18	39·948	Francium (Fr)	87	(223)
Arsenic (As)	33	74·9216	Gadolinium (Gd)	64	157·25
Astatine (At)	85	(210)	Gallium (Ga)	31	69·72
Barium (Ba)	56	137·34	Germanium (Ge)	32	72·59
Berkelium (Bk)	97	(247)	Gold (Au)	79	196·967
Beryllium (Be)	4	9·0122	Hafnium (Hf)	72	178·49
Bismuth (Bi)	83	208·980	Helium (He)	2	4·0026
Boron (B)	5	10·811	Holmium (Ho)	67	164·930
Bromine (Br)	35	79·904	Hydrogen (H)	1	1·00797
Cadmium (Cd)	48	112·40	Indium (In)	49	114·82
Cesium (Cs)	55	132·905	Iodine (I)	53	126·9044
Calcium (Ca)	20	40·08	Iridium (Ir)	77	192·2
Californium (Cf)	98	(251)	Iron (Fe)	26	55·847
Carbon (C)	6	12·01115	Krypton (Kr)	36	83·80
Cesium (Ce)	58	140·12	Kurchatovium (Ku)	104	(260)
Chlorine (Cl)	17	35·453	Lanthanum (La)	57	138·91
Chromium (Cr)	24	51·996	Lawrencium (Lw)	103	(257)
Cobalt (Co)	27	58·9332	Lead (Pb)	82	207·19
Copper (Cu)	29	63·546	Lithium (Li)	3	6·939
Curium (Cm)	96	(247)	Lutetium (Lu)	71	174·97
Dysprosium (Dy)	66	162·50	Magnesium (Mg)	12	24·312
Einsteinium (Es)	99	(254)	Manganese (Mn)	25	54·9380

*In parentheses is given the symbol of each element.

†Values in parentheses are mass numbers of the most stable or the best known isotopes.

Element	Atomic Number	Atomic Mass	Elements	Atomic Number	Atomic Mass
Mendelevium (Md)	101	(256)	Ruthenium (Ru)	44	101·07
Mercury (Hg)	80	200·59	Samarium (Sm)	62	150·35
Molybdenum (Mo)	42	95·94	Scandium (Sc)	21	44·956
Neodymium (Nd)	60	144·24	Selenium (Se)	34	78·96
Neon (Ne)	10	20·183	Silicon (Si)	14	28·086
Neptunium (Np)	93	(237)	Silver (Ag)	47	107·868
Nickel (Ni)	28	58·71	Sodium (Na)	11	22·9898
Niobium (Nb)	41	92·906	Strontium (Sr)	38	87·62
Nitrogen (N)	7	14·0067	Sulphur (S)	16	32·064
Nobelium (No)	102	(254)	Tantalum (Ta)	73	180·948
Osmium (Os)	76	190·2	Technetium (Tc)	43	(99)
Oxygen (O)	8	15·9994	Tellurium (Te)	52	127·60
Palladium (Pd)	46	106·4	Terbium (Tb)	65	158·924
Phosphorus (P)	15	30·9738	Thallium (Tl)	81	204·37
Platinum (Pt)	78	195·09	Thorium (Th)	90	232·038
Plutonium (Pu)	94	(242)	Thulium (Tm)	69	168·934
Polonium (Po)	84	(210)	Tin (Sn)	50	118·69
Potassium (K)	19	39·102	Titanium (Ti)	22	47·90
Praseodymium (Pr)	59	140·907	Tungsten (W)	74	183·85
Promethium (Pm)	61	(147)	Uranium (U)	92	238·03
Protactinium (Pa)	91	(231)	Vanadium (V)	23	50·942
Radium (Ra)	88	(226)	Xenon (Xe)	54	131·30
Radon (Rn)	86	(222)	Ytterbium (Yb)	70	173·04
Rhenium (Re)	75	186·2	Yttrium (Y)	39	88·905
Rhodium (Rh)	45	102·905	Zinc (Zn)	30	65·37
Rubidium (Rb)	37	85·47	Zirconium (Zr)	40	91·22

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University General Chemistry

An Introduction to Chemical Science

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येनावृतं नित्यमिदं हि सर्वं ज्ञः कालकारो गुणी सर्वविद् यः ।
तेनेशितं कर्म विवर्ततेह पृथिव्यप्तेजोनिलखानि चिन्त्यम् ॥

*Keep in mind that, commanded by Him who is pure conscious-
ness, (who is) all knowing, (who is the) maker of time, in
whom all qualities reside and who ever envelopes all this,
energy (action) manifests itself as earth, water, light, air
and space.*

Svetasvatara Upanishad
6 Adhyaya, Verse 2

*You learn science by keeping your eyes and ears open and
looking around at this world; the whole world bristles with
problems to solve.... The real inspiration of science, at least
to me, has been essentially the love of nature.... The essence of
scientific spirit is to look behind and beyond and to realise what
a wonderful world it is that we live in. Everything that we see
presents to us not a subject of curiosity, but a challenge to the
spirit of man to try to understand something of this vast mystery
that surrounds us.*

C V Raman

Preface

Chemistry has seen its greatest information explosion in the last decade and college curricula are becoming increasingly inadequate to cope with the flood of new ideas and information. There appears to be general agreement that courses in chemistry should be restructured in such a way as to present unifying principles of chemistry. This unification is particularly essential in presenting chemistry to beginners. The traditional substructure of physical, organic, inorganic, and analytical chemistry has origins in the main activities of chemists in the past, but still continues to determine how chemistry is taught. However, it does not accurately reflect or encompass what is actually done in chemistry. Chemistry today is dynamic in scope and chemists find themselves working in areas currently described as interfaces like molecular biology or solid state science. These interfaces progressively get absorbed and become integral parts of chemistry. Chemistry has truly developed into chemical science and people trained as chemists are making significant contributions in areas which overlap strongly with physics, biology as well as earth and materials sciences. As such, any organisational scheme to provide unified instruction in chemistry should recognise the strong interaction between the various branches of chemistry and the increasing exchange of ideas between chemistry and other sciences.* A syncretic course in general chemistry given during a student's first year in college would go a long way in providing the right perspective of chemistry.

The need for formulating a general chemistry curriculum suited to beginning college students in this country was recognised sometime ago by the Chemistry Panel of the National Council for Science Education, New Delhi. The panel organised a national symposium on this topic at the Indian Institute of Technology, Kanpur. Besides enthusiastically endorsing the introduction of general chemistry courses at the beginning college level, the symposium made recommendations regarding the curricular content. As a follow-up action, the National Council for Science Education sponsored a Curriculum Development Group to prepare a textbook of general chemistry and this text is the result of the effort of the group.

In providing unified presentation of chemistry, one can think of several ways of organising a general chemistry course. There has been the attractive suggestion that chemistry be subdivided into the areas of structure, dynamics and

*Chapter 1 of this text on the structure and scope of chemical science, particularly the 'landmarks in science' listed at the end of the chapter, brings out this aspect clearly.

synthesis; unfortunately, this subdivision does not appear to maintain the unity of well-organised subjects like chemical thermodynamics, solid state chemistry and so on. Another subdivision could be structure and physical properties of pure substances, chemical transformations, and application of chemistry to complex systems. Obviously, as Kipling said ' there are nine and sixty ways of constructing tribal lays. And-every-single-one-of-them-is right '.

The contents of this text can be classified under the broad headings, structure, energy and transformations. Thus, Chapters 2 to 8 cover structure and properties of systems, Chapters 9 to 12 on thermodynamics and equilibria deal with energy; Chapters 13 to 17 deal mainly with transformations in inorganic and organic systems, although some of them also include considerable structural information. Chapter 18 dealing with biological systems is essentially a complete unit by itself and contains all the three components. All through the book, the underlying theme has been the chemists' molecular or microscopic approach as pointed out in Chapter 1. The detailed treatment of atomic and molecular structure in Chapters 2 to 4 should indeed provide a sound basis for the study of chemical systems. A particularly significant feature of the book is the emphasis on the classical atomic-molecular theory in Chapter 2, based on the structureless atom; the classical treatment of structure is important to appreciate since chemistry did advance considerably much before the discovery of the electron. We have thus preferred to classify modern atomic-molecular theory as the one which developed after the discovery of the electron. We have tried to bring in other novel features in the treatment of various topics, although it is becoming increasingly difficult to do so due to the large number of good textbooks on general chemistry published in recent years. We have in fact benefited immensely by the approaches of several authors of general chemistry in the preparation of this text. This book is a departure from traditional chemistry texts in this country which generally overemphasise descriptive chemistry and often demand excessive memorisation on the part of the student. We are of the view that a student's curiosity about chemistry is kindled not merely by describing chemical behaviour, but by suitably pointing out the relevant principles which make the behaviour possible.

In order to make the text truly one on general chemistry, we have stressed the interplay among the various traditional divisions of chemistry as much as possible and in so doing, we have included a variety of examples from inorganic, organic and biological systems. For example, in the chapter on chemical kinetics, in addition to covering a number of examples of organic, inorganic and biological reactions, we have also touched on the problems of the environment. We have introduced organic molecules in the early part of the text, immediately after molecular structure, in order to be able to use organic substrates in our examples; this is indeed a departure from most texts in general chemistry. In addition to illustrating the applications of principles of chemistry with examples, we have attempted to show how chemistry works for man. For example, we have dealt with several organic chemical processes of importance in some detail. While dealing with solids, we have shown the importance of solid materials in the modern world. We have discussed the chemistry of the living cell in some detail to answer the increasing interest in this area.

We believe that this book will serve as a good introductory text in chemistry after higher secondary school, pre-university course or intermediate college training. By its very nature, the book can be used not only by those specialising

in different branches of science, but also in engineering, agriculture, or medicine. With this background, a student will have a sound knowledge of the principles of chemical science which can be applied in any situation. Although we have maintained the treatment of the subject matter quite quantitative, the discussion in the text is not very mathematical and we believe that lack of mathematical background will not be a serious impediment to the study of the text. We have considered it better to use the conventional units generally employed in chemistry instead of the SI units at this stage (except for mol standing for mole); we have, however, included an appendix on the SI units at the end of the book. Hopefully, future editions of the book will be in SI units.

It is often said that no more than 50 per cent of a textbook is covered in a course. This may be equally true of this text. The material here has been covered in sufficient detail so that there are enough alternatives in the choice of material and depth of coverage for any given course in general chemistry. We believe that teachers can readily adjust the course depending on the requirements and the time available. We also think that by an appropriate choice of the material in the text, a sound general chemistry course can be offered to any batch of students at any desired level of sophistication. Further, a general, chemistry course at this level can be offered by any chemistry teacher without need for expertise in any specific area. At the Indian Institute of Technology Kanpur, this text has been used for a two-semester course involving about ninety lectures (three lectures a week) and sixty tutorials (two tutorials a week).

We feel that most students should be able to read this text on their own. Some of the material in the text in small print is intended as extra reading for the more inquisitive students. The books listed at the end of each chapter would also be of value in this regard. We have worked out a large number of examples in order to make the presentation quantitative and we hope that these will provide the necessary incentive for a proper study of the subject.

Any general chemistry course will have to be associated with a sound laboratory programme and we believe that a good choice of experiments can be found in the book by Rao and Agarwala. As such, we have not listed any suggestions for experiments as part of the text.

We have enjoyed preparing this text and we hope that it will serve as a catalyst to students in the study of chemical science and to our colleagues in teaching general chemistry. We shall feel more than rewarded if this book serves to encourage the teaching of general chemistry as the first course at college level. It is possible that there are typographical and other errors which might have escaped our notice and we shall welcome all suggestions for improvement.

C N R Rao

The devil may write chemical text books because every few years, the whole thing changes.

J J Berzelius (1779–1848)

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UNIVERSITY
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1

Structure and
Scope of Chemical Science

What distinguishes the language of science from language as we ordinarily understand the word? How is it that scientific language is international? ... The super-national character of scientific concepts and scientific language is due to the fact that they have been set up by the best brains of all countries and all times.... Their system of concepts has served as a guide in the bewildering chaos of perceptions, so that we learned to grasp general truths from particular observations....

What hopes and fears does the scientific method imply for mankind? I do not think that this is the right way to put that question. Whatever this tool in the hand of man will produce will depend entirely on the nature of the goals alive in this mankind. Once these goals exist, the scientific method furnishes means to realise them. Yet it cannot furnish the very goals. The scientific method itself would not have led anywhere, it would not even have been born, without a passionate striving for clear understanding.

ALBERT EINSTEIN

In just about two hundred years since it emerged as a systematic science,* chemistry has made impressive contributions to human knowledge and civilisation. The ingenuity of millions of chemists the world over has brought about an increasingly fundamental understanding of the nature, composition, and behaviour of matter. This understanding is not only a source of intellectual satisfaction but it has also contributed directly or indirectly to the silent technological revolutions in agriculture, communication, medicine, metallurgy, public health, textiles, transportation, and countless other fields. In this book,

*It is difficult to pinpoint the birth of any subject. However, it is generally agreed that the last quarter of the 18th century witnessed many developments which contributed to the beginning of systematic chemistry. It was during this period that oxygen was discovered, phlogiston theory was discredited, and the important phenomenon of combustion was understood. The French Chemist Antoine Lavoisier, whose classic researches were carried out during this period, is commonly regarded as the Father of modern chemistry.

we shall only deal with the fundamental aspects of chemistry with special emphasis on those conceptual approaches which provide a unified and a rational description of chemical phenomena.

The statements made above concerning the contributions of pure and applied chemistry should not be taken to mean that other branches of science and engineering have played no role in these advances. Major progress in a particular area often comes only through the combined knowledge gained from several disciplines. Similarly, a major breakthrough in a subject seldom remains confined to that particular subject. It is, therefore, pertinent to enquire into the relationship of chemistry to some of the sister sciences like physics and biology but before doing this we shall briefly look into the nature of the scientific method which is common to all branches of science.

1.1 NATURE OF THE SCIENTIFIC METHOD

The territory of science sweeps across the entire range of phenomena taking place in space and time. From the tiniest fundamental particle (size of the order of 10^{-14} cm) to the entire universe (size of the order of billion light-years*), from time spans as large as 10^{10} years (approximate age of the universe) to time intervals as small as 10^{-24} seconds (time taken by light to traverse a nucleus), from inanimate matter to that ' most wonderful lump of matter in the universe—the human brain ', all come within the domain of science. What is the method by which scientists seek to rationalise and understand these phenomena? Fortunately or unfortunately there is no unique method which when mastered will enable a person to solve all problems in science. Great ideas in science are the product of creative flashes of human mind, and scientific creativity, like artistic creativity, defies analysis. However, there does exist a broad framework within which all scientists operate. This is useful to communicate and evaluate scientific work but is of no value as a prescription for making a great discovery. This framework may be called the scientific method.

The role of observation and reasoning in everyday life: The methods used by scientists have evolved from methods used in everyday life. In dealing with day to day events, two of our common tools are observation and reasoning.† Let us take a simple example to illustrate this point. What does one do when on pressing the light switch in a room, it is observed that the electric bulb does not light up? Normally, the actions that follow like replacing the bulb or checking the fuse-box are done quite mechanically, but let us analyse the reasoning involved since each step in this analysis has a counterpart in scientific method. First of all, on observing that the bulb does not light up, we believe that there exists a reason for this occurrence. We have got used to the ' cause and effect ' relationship between the pressing of the switch and the lighting of the bulb and we are not prepared to discard it just because of one instance. In the same way scientists believe that all natural phenomena are interconnected by cause and effect in such a manner that the same cause

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*A *light year* is the distance covered by light (speed 3×10^{10} cm per second) in one year. This distance is of the order of 10^{18} cm.

†It has been said that intuition is nothing but reasoning in a hurry!

always produces the same effect. There is no *a priori* justification for this belief; it is only that science exists and has made progress because of the faith in a causal and rational universe. This means that just as we do not hold divine intervention responsible for the failure of the bulb to light up, a scientist also prefers to investigate every phenomenon rather than invoke mystical spirits.

Going back to the switch and bulb case, let us now find an explanation. The simplest hypothesis is that the bulb is burnt out. We can verify this by observing the bulb. If the bulb has an opaque coating, direct observation is not possible. We then check our observation indirectly by replacing the bulb. If the new bulb works, the problem is solved; if it does not, we discard our hypothesis and start all over again by taking other steps like seeing whether the fan in the room works and if it does not, whether the fuse has blown out and so on. The method of a scientist is very similar. On observing some phenomenon he will think of a tentative explanation. If the explanation can be directly tested, the matter is simple; if not, he goes about testing it indirectly. Every successful test increases his confidence but a single unsuccessful test invalidates the ' explanation ' and he has to start all over again.

The steps outlined above are necessary in any scientific investigation but they are by no means sufficient. One cannot spell out any rules about what to observe or how to observe. Similarly, though a particular line of scientific reasoning can be unambiguously tested, no guidelines can be provided as to how to think of an explanation in the first place. Here, not only knowledge but also imagination, intuition, vision, etc., play an equally important role. These intangible parts of science constitute its creative element and they are a source of constant delight to a scientist. They are also a source of constant frustration to a scientist in his not so creative moments!

In a nutshell then, scientific method is organised commonsense based on observation and reasoning. The scientist has taken these two tools from daily life and sharpened them to make them useful for probing nature. These tools in the scientific terminology are usually known as experiment and theory. Let us briefly look at some of their characteristics.

Nature of experiment: An experiment is a controlled observation. Experiments can be qualitative involving only observation or they can be quantitative involving measurements. Thus, one can put salt in water and watch it dissolve or measure the amount of salt dissolving in water to determine the rate of dissolution and the amount in solution. To carry out an experiment, a scientist may need specific apparatus which he often builds depending on the requirements.

Experiments lead to classification and generalisation which are the first steps in perceiving order and regularity in the phenomenon under study. Thus, experiments suggested the solid–liquid–gas as well as the element–compound–mixture classifications, which have facilitated the study of chemistry enormously. Experiments involving measurements yield quantitative regularities. For example, Robert Boyle's classic investigations on gases uncovered the fact that the volume of a given mass of gas is inversely proportional to the pressure at a constant temperature. It is usual to present the findings of an experiment in the form of tables, graphs, and mathematical equations, which summarise the observed data. Experimental findings of major importance are often

designated as 'laws',* e.g. we have the law of constant composition in chemistry, Ohm's law in physics and Mendel's law of genetics in biology. It should be realised that an experimental law is a concise statement of the regularity observed in a particular phenomenon; it does not constitute an explanation of the phenomenon. Thus, the constant composition law, Ohm's law or Mendel's law does not provide any answer as to why the phenomenon it describes shows that particular behaviour.

The nature of theory: The task of a theory is to find deeper correlations in observable behaviour and experimental laws. Some of the outstanding theories of science are Dalton's atomic theory, Newton's theory of mechanics, Einstein's theory of relativity, and Darwin's theory of evolution. All such theories comprise the following parts: (*a*) a set of unproved statements which form the starting point and are variously known as assumptions, hypotheses, postulates, or axioms;† (*b*) a set of statements which follow from the assumptions through logical reasoning and are variously known as deductions, conclusions, or theorems; and (*c*) definitions which define the terms occurring in the assumptions and the conclusions. This can be illustrated by two simple examples:

Assumption:	All flowers are fragrant
Definition:	Rose is a flower
Conclusion:	Rose is fragrant

Assumption:	Atoms have mass and they are indestructible
Definition:	Chemical reactions are rearrangement of atoms
Conclusion:	Mass is conserved in chemical reactions

Theories satisfying the above requirements are found in mathematics as well (e.g. group theory, theory of complex variable). But there is an important difference between a mathematical theory and a scientific theory. In the former, the only requirement for a theory to be valid is internal consistency between the assumptions and the conclusions while in the latter, apart from internal consistency, it is necessary that the conclusions agree with experiments. This means that whereas a consistent mathematical theory is timeless, scientific theory, even if it is consistent, may have to be revised if its conclusions contradict some new experiment. Lack of appreciation of this point frequently confuses beginners. For example, Dalton's atomic theory based on the assumption of the indestructible atom served chemistry and physics throughout the 19th century but when experiments established that atoms are divisible, Dalton's theory had to be revised.

The progress of science is marked by periodic replacement of older theories by newer ones. This situation tempts one to conclude that there is no point in studying scientific theories since they are notoriously transient. Such a conclusion betrays a total misconception about the nature and the utility of a theory. While it is true that there is no guarantee that a scientific hypothesis will stand

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*For historical reasons, the term 'law' is also used to designate some theories, e.g. 'laws of motion' or 'laws of thermodynamics'. The modern trend is not to use this term in theoretical contexts.

†We shall treat all these terms as equivalent even though some scientists prefer to draw out finer distinctions between them.

the test of time, a theory remains useful as long as it can make reliable predictions. When experiments force a revision, it rarely happens that the older version is completely discredited. What usually happens is that the earlier theory is generalised to deal with the new situation and the older theory continues to be useful either as a stepping stone to the new theory or as a description valid only for restricted and special situations. Two examples will clarify this point. When Bohr's theory of atomic structure came in conflict with the experimental findings, it was replaced by the quantum mechanical theory of atomic structure. Though the latter overhauls many of the older ideas, it does leave some of them intact. Moreover, Bohr's theory is very useful as an introduction to the more abstract and difficult ideas of the newer theory. Our second example pertains to Dalton's theory. When scientists succeeded in splitting an atom, Dalton's concepts certainly had to be modified but this did not mean that the Daltonian ideas had become totally useless. In a vast majority of chemical reactions, atoms suffer only minor internal rearrangement and consequently many (but not all) features of chemical behaviour can be adequately explained on the basis of indestructible atoms.

Scientific theories can be qualitative, like Darwin's theory, or quantitative, like Einstein's theory. A quantitative theory is naturally more precise since it provides not only an understanding but also numerical estimates. Thus, Darwin's theory only qualitatively accounts for the origin of species, but Einstein's theory, besides pointing to the connection between mass and energy, enables one to compute the amount of energy contained in a given mass. Though the aim of every branch of science is to evolve quantitative theories, in many areas the complexity of the situation often requires scientists to be satisfied with qualitative explanations only. A good example is the problem of weather. The principles underlying various aspects of this problem, like the formation of clouds, the origin of lightning, the occurrence of monsoon, cyclones, or typhoons are well understood. Nevertheless, it is not feasible at present to predict precise weather conditions in advance because the detailed computations involved are enormously complex. Contrast this with the following situation. The principles of planetary motions are also well understood but here the theory is quantitative since the relative simplicity of the problem permits accurate computation. Consequently such phenomena as eclipses, sun-rise, or the phases of moon can be precisely calculated in advance. We shall see later that existing chemical theories fall under both categories. One of the major efforts in modern chemistry has been to replace the qualitative theories by their quantitative versions.

Role of concepts and models in science: In formulating and communicating experiments as well as theories, scientific concepts play a pivotal role. Some common examples are the concepts of temperature, pressure, energy, element, compound, molecule, orbital, chemical bond, and so on. Scientific concepts are created on the one hand to express experimental findings; on the other hand, by grouping together several concepts in the form of a theory, they are used to explain experimental results.

It is of interest to examine the way we invent and use concepts in daily life. The five senses of man—sight, sound, smell, touch, and taste—are his five windows to the external world. To comprehend and to communicate daily events, we make use of a language. Each language has a vocabulary in which a particular word expresses a particular idea. An idea can refer to some-

thing concrete or something abstract. For example, the word 'house' denotes an object which the word 'beauty' stands for an abstract notion. In the same manner, a scientist comprehends and describes nature by using words which express ideas. For the most part, the words of science are taken from those in daily usage. However, invariably the ideas they refer to are more precise. For example, the terms 'pressure' and 'energy' have a precise connotation in science whereas they are rather vaguely interpreted outside science. Sometimes situations arise where none of the common words describe a concept properly. It then becomes necessary to coin new words. 'Molecule' and 'orbital' are two of several examples of this type.

A large number of scientific concepts can be defined by definite experimental procedures. Such a definition is called an operational definition of the particular concept. The concepts of 'mass' and 'heat of reaction' belong to this category since they are identified with experimentally determinable quantities. However, a concept can be scientifically acceptable even if it is not directly measurable so long as it can be related through other concepts to some observables. For example, the instantaneous rate of a reaction cannot be measured since any measurement must be spread over a finite duration. Nevertheless, the rate of reaction is a respectable and useful chemical concept because it can be related to average rate, a directly measurable quantity. Concepts which cannot be defined either directly or indirectly in terms of observables are considered unscientific concepts.*

Sometimes it is said that a scientific theory provides a conceptual model— or simply a model—for a particular phenomenon. Thus, we use expressions like 'kinetic model of a gas' or 'planetary model of an atom'. Such experssions are used in the following sense. We infer the behaviour of atoms in a gas or of electrons in an atom through abstract reasoning. Quite often it so happens that one or more aspects of this behaviour has an analogy on the macroscopic, visible scale. For example, according to the kinetic theory of gases, atoms seem to behave as if they are hard billiard balls. Many facts about gaseous behaviour like the relation between pressure, volume and temperature, can be obtained by treating atoms like billiard balls. Similarly, in the Bohr theory of the hydrogen atom, the roles of the electron and the nucleus are analogous to that of planets and the sun; hence the origin of the term 'planetary model of atoms'. However, this does not mean that an atom is a billiard ball or an electron is a planet in every respect. Models and analogies are of invaluable help in visualising many phenomena but they must be judiciously used. Some of the greatest ideas in science have originated from models and analogies. A famous example is Kekule's suggestion of a hexagonal ring structure for benzene which was one of the most important events in early organic chemistry. This type of structure occurred to Kekule when he saw, in a dream, a snake curling onto itself.

Limitation of the scientific method: The methodology of science discussed above provides the common thread which binds together all the sciences. Let us now discuss some of the areas where the scientific method has been most successful. Although, in principle, the method can be used to analyse any phenomenon, in practice, its applicability is restricted to those problems where it is possible to design and perform experiments. This limitation forces many

*If a concept is unscientific, it does not mean it is bad. Honesty, truth and love are amongst many of the 'good' but unscientific concepts.

important facets of human experience like emotions, creativity, ethics, and perhaps the most fundamental of all questions, the meaning and purpose of life, to lie outside the range of scientific investigation. Until and unless these limitations are overcome, it can be justifiably said: ' Man cannot live without science, but he cannot live with science alone'. However, it should be realised that one cannot and should not put any *a priori* limitation on the scientific method. It has repeatedly happened that experiments which were thought ' impossible ' in a particular age, have become possible in another age, thus enlarging the domain of science. For example, only in the 17th century, a famous philosopher said: ' Man will never know the true nature of planets since he is destined to live and die on earth '. But within two hundred years, scientific progress put a man on the moon thus opening a whole new area to science.

The different branches of science are distinguished mainly by the fact that they investigate different aspects of natural phenomena. In some branches experiments can be carried out, but they are not precise because controlled observation is not possible. This is frequently the case in social sciences like economics or behavioural sciences like psychology and hence scientific investigations in these fields have had a tentative character. In biological and even more so in physical and chemical sciences, experiments are becoming increasingly precise with the result that theories can be formulated and tested with increasing exactness.

1.2 STRUCTURE OF CHEMICAL SCIENCE*

Scope of chemical science: A discussion of the structure of chemical science requires definition of the subject and its scope. A reasonable short definition of the scope of chemistry has been given as: *Chemistry is the integrated study of the preparation, properties, structure, and reactions of the elements and their compounds, and of the systems which they form.* Interpreted in the broadest sense, this definition would include most of natural science, a consequence of the considerable areas of overlap which chemistry has with physical, biological, earth, and material sciences.

Chemists, as compared to physicists, tend to work on molecular rather than atomic systems, and on molecular structures and transformations rather than on phenomena associated with simple substances only. Compared to biologists, chemists are generally interested in the details of the structure and properties of the molecules of the living cell, rather than in the operation of cell and collections of cells. Chemistry is thus uniquely a *molecular science* and the approach of chemists in understanding natural phenomena is almost always concerned with molecular models.

Chemical science is dynamic in scope and many chemists find themselves working in areas currently described as interfaces (for example, molecular biology and solid state physics). Some of the most exciting areas of research today are in these changing interfaces with other disciplines. These interfaces are often absorbed and become integral parts of chemical science. Examples are nuclear chemistry, quantum mechanics, statistical mechanics, magnetic

*We have closely followed the report of the International Conference on Education in Chemistry, Colorado, USA, July 1970, in writing this section.

resonance, biochemistry, solid state chemistry and geo- and cosmo-chemistry. As a consequence, those subjects considered central to chemical science change significantly with time. It, therefore, appears detrimental to define the scope of chemistry narrowly, since to do so would restrict chemical science from developing in important nontraditional areas. In fact, the fantastic ability of chemists to extend their activities into other areas of science is evidence of the vigour and vitality of the subject.

A very important aspect of chemical science is the use of chemistry in the analysis and modelling of complex systems. It is possible that in the future some people may prefer to call themselves ' systems chemists'.* The behaviour of complex systems like a rocket motor, a living cell, or a polluted atmosphere, depends critically on chemical properties and processes. Combination of the increasing competence of both chemical and systems analysis will make these tools more and more compatible for attacking some of the most challenging problems of man.

Theory and experiment: Since the structure and growth of chemistry have been strongly influenced by the patterns of thought in the theories of chemistry, it becomes necessary to examine the role of theory and experiment in chemistry. In chemistry, whether the goals are the synthesis of a new compound or the investigation of properties or principles, all investigations generally have a theoretical basis. This is, of course, nothing but the application of the scientific method. The way in which chemistry differs from other sciences lies in the nature of the theories.

The underlying basic theory of chemistry, namely the molecular basis of the subject, is well-established. Interactions between constituent particles in molecules are governed by the laws of quantum mechanics and the properties of large aggregates at a molecular level are described by statistical mechanics. Transformations on a macroscale follow the laws of thermodynamics. The difficulty in applying these laws to real situations, however, often renders them of marginal value for practicing chemists. They then proceed to adopt mental constructions (models) to guide their thinking. These may be quantitative (and mathematical) or only qualitative. The really charcteristic features of a chemist is his ability to make these models experimentally productive in terms of giving them some measure of physical significance and serving the useful role as guides for making verifiable predictions. This does not mean that chemists undermine the study of the correlation between *a priori* theory and experimental results; this forms an integral part of the structure of chemistry.

It is immaterial whether or not a particular model has lasting merit. Thus, a rejected theory like the phlogiston theory has value in the development of the subject as long as it provides a satisfactory correlation of available experimental data and enables further experimentation. The value of models is also in providing quick and ready answers. For example, if one wishes to guess the shape of a molecule, the electron pair repulsion model rightaway gives the answer. However, one should be careful in not pushing a simple model too far in order to obtain better agreement with experimental results. It is interesting, however, that many accidental or novel discoveries arise from results which conform poorly with the model employed.

*The concept derives from systems analysis, an approach now associated primarily with engineering science.

Too much stress or attention on a single model may seriously inhibit chemical advances. It is said by some that the factor which distinguishes a chemist from a physicist is that the former argues from 100 weak facts, whereas the latter argues from one strong fact. We must concede that chemistry is possibly less straightforward than physics. Molecular properties are inferred from indirect measurements and evidence from many different sources becomes essential.

While models play a crucial role in chemistry, they are by no means the most esteemed outcome of efforts in chemistry. The model is the *sine qua non* of an advance in a field, but has no value except in the context of facts that it correlates. A scientist cannot, however, grasp the significant flavour of any model without considering some of the facts.

Substructure of chemistry: The traditional substructure of physical, organic, inorganic, and sometimes analytical chemistry has origins in the past activities of chemists and still continues to determine how chemistry is taught. However, it does not accurately reflect or encompass what is actually done in chemistry. Today, biochemistry is establishing itself almost as a separate discipline. Further, people trained as chemists are frequently making significant contributions in areas which overlap strongly with physics, biology, and earth and materials sciences.

The strong interaction between various branches of chemistry indicates the need for other organisational schemes which would aid in the unified instruction in chemistry, reduce parochialism and increase exchange of ideas among chemists and other scientists. The suggestion that chemistry be subdivided into the areas of structure, dynamics, and synthesis provides an attractive opportunity to encourage a broader viewpoint, but unfortunately, this does not maintain the unity of well-organised subjects like chemical thermodynamics, or accommodate newer areas like solid state chemistry and macromolecular chemistry. Another possible subdivision would be the following: the structure and physical properties of pure substances, chemical transformations, and the application of chemistry to complex systems. Spectroscopy, diffraction and other structural methods would fall into the first area along with the study of such things as phase transitions and thermal, magnetic and electrical properties. The subject of chemical transformations would include reaction kinetics, thermodynamics and synthetic methods. Application of chemistry to complex systems would include such fields of current activity as molecular biology, materials science and geochemical phenomena.

1.3 CHEMICAL SCIENCE IN THE SERVICE OF MAN

The most significant aspect of modern science is the impact it has had in solving a variety of problems of practical and technological importance as well as those related to the pressing problems of mankind. A large number of these problems require a proper understanding and application of chemical principles and processes. Before examining how chemistry has worked for man, we shall briefly look at some of the challenging problems of this generation.

The major threats to the present day civilisation are population explosion, hunger and disease, environmental pollution, depletion of sources of energy as well as natural resources. Of these, the growth of population is probably the greatest problem facing us since this in turn determines how well we can

tackle and solve the others. The rate of growth of human population is today about 2 per cent per year (compared to 0·04 per cent not too long ago). This rate of growth doubles the population in about thirty-five years. With this kind of growth, we are fast depleting the nitrogen and oxygen in air, both of which are essential for life.* In addition, we are continually polluting air and water. The quantity of fresh water for sustaining human life is getting reduced in many parts of the world and there is increasing need for new sources of fresh water.

The food problem is getting to be more and more acute and there will soon be little world surplus available for redistribution unless there is population control or/and major agricultural reforms in most parts of the world. This is particularly so in the case of some developing countries. Even as scientists are finding cures for most illnesses and diseases, the minimum medicare and health are yet to be provided to a vast majority of the developing world.

Man is fast exhausting all the known reserves of energy. While he may turn to nuclear and solar energy for some relief, it is important to know that by the year 2100, the rate of energy generation by man on earth will exceed the present rate of energy retention from the sun and there will be a major energy deficit in the world. (After all, most of the useful energy on earth comes from the sun.) By this time, the world population will reach around sixty billion and there would hardly be sufficient space on land to accommodate this population.

In solving most of these pressing problems, chemists have a lot to do. There is need for newer and better birth control chemicals. Syntheses of newer drugs are to be carried out; as Paracelsus (1493–1541) said ' the true use of chemistry is not to make gold, but to prepare medicines '. Chemists have to work on newer sources of food and nutrients. Desalination of sea water should be made ·economically feasible. Then, there is the problem of atmospheric pollution, if and when it is solved will only be done through an understanding of chemical dynamics. Having indicated the nature of involvement of chemists in real life problems, we shall now briefly discuss a few of the specific areas in some detail.

Drugs: Substances from natural sources have been used since antiquity for treatment of disease. For example, an extract from the bark of poplar, olive, or willow trees was recommended more than two thousand years ago by Hippocrates—the father of medicine—for treating fever. The difference between the ancient and modern approach to the problem of remedial drugs is that whereas one had to be satisfied earlier with impure substances, one can now isolate and purify the drug from natural source and establish its chemical structure. If the substance is sparsely occurring, chemists can synthesise it, thus making it widely available. Even more impressive is the ability of chemists to produce by synthesis enitrely new drugs not occurring in nature.

The active principle of the fever-reducing extract mentioned above was identified by chemists as salicylic acid. It was, however, found that the acetyl derivative of this is more potent for alleviating pain and controlling fever. Acetyl salicylic acid, called *aspirin* is one of the earliest examples of a synthetic

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*At the present rate of cycling there is sufficient nitrogen and oxygen for 10^{10} people which is only three times the world's population.

drug, and in its parent or modified form, it is one of the most widely used drugs. Another notable early example of a synthetic drug is *salvarsan* which in chemical language is 3, 3'-diamino-4, 4'-dihydroxy arseno-benzene. Paul Ehrlich, the German chemist, was searching for a cure for the dreadful disease syphilis and succeeded after no less than 605 failures. Beginning with this there has been a veritable deluge of synthetic and natural drugs that chemists have given to medicine. Prominent among these are the *sulpha drugs* (prontosil), *antibiotics* (penicillin, streptomycin, chloromycetin), *anti-malarials* (quinine), and *anaesthetics* (chloroform, cyclopropane). Mention must also be made of the wonder drug *cortisone*, which has brought relief to millions suffering from rheumatoid arthritis and rheumatic fever.

Food: Shortage of food is one of the serious issues facing more than half of the world. Though primarily an agricultural problem, chemists are also contributing towards its solution. Firstly, by developing synthetic *fertilisers* (calcium superphosphate, potassium and ammonium nitrate, etc.) chemists have provided to the plants in generous amounts the three elements—phosphorous, nitrogen and potassium—essential for their growth. Elements like zinc and cobalt which are needed in trace amounts are also added as chemicals to correct special mineral deficiencies in soils.

Higher yield of crops, however, does not depend upon fertilisers alone. The crops have to be protected from insects, weeds, bacteria, viruses, and fungi. This is done by an army of man-made chemical soldiers like synthetic *insecticides* (e.g. DDT, malathion), *weed killers* (2, 4-D), and *fungicides* (chloranil). Chemists are now working on insect hormones for controlling insect populations. In many countries, farmers use laboratory-made chemicals as *defoliants*. For example, magnesium chlorate when applied to ripened cotton crop causes the leaves to fall off thus making harvesting much cheaper and faster. The chemists are also trying to control the maturity of different plants which will enable farmers to spread the harvesting and processing time of different crops. The control of pineapple crop has been successfully achieved with naphthalene acetic acid.

Chemicals are also used extensively in animal farming. Apart from correcting dietary deficiencies, synthetic substances are used to protect animals from diseases. For example, the new insecticide ' marlate '—used as a dip or as a spray—kills blood-sucking hornflies which attack cows. This step alone leads to 10 per cent increase in milk supply.

Fuels: Until recently, the only fuels known to mankind were naturally occurring substances like coal, coke, marsh gas (methane), wood, etc. Processing of petroleum has completely changed the situation. Crude oil which is found deep inside the earth is a mixture of many hydrocarbons and several impurities like wax, clay, and sulphur compounds. Chemical techniques are first used to purify the oil and then to separate hydrocarbons into several groups. The heavier hydrocarbons are ' cracked ' into lighter ones which form the main components of gasoline fuel. Different grades of gasoline are used in automobiles, aviation and so on.

The importance of the *petrochemical* industry is also due to the fact that it contributes a very large number of useful chemicals like benzene, toluene, xylene and naphthalene. Petrochemicals provide the base for manufacture

of synthetic fibres, synthetic rubber, fertilisers, resins, detergents, refrigerants and explosives.

Fibres: Ancient civilisations like in India and China were well known for producing exquisite varieties of cotton, silk and wool from natural sources. In recent years, synthetic chemistry has entered this field with products like *nylon*, *rayon* and *terylene*. These man-made *fibres* rival, and in some respects excel, the natural fibres. They are longer lasting, crease resistant, and quick drying.

Besides the above areas, there are many other frontier and interdisciplinary areas where the contribution of chemists is significant. Chemists with their knowledge of materials and methods are basically materials scientists who can produce tailor-made materials with desired properties. The materials include glasses and ceramics, electronic, magnetic, and optical materials, fibre-based composites (with high strength and light weight), etc., and the applications of these materials will range from fisherman's boat to digital computers. *Desalination* of water involves a study of the physico-chemical aspects of membranes. In the area of *environmental pollution*, chemists are finding better methods of analysis and solutions to get rid of pollution. There is the entire area of *marine chemistry* to investigate the new sources for food and chemicals. Chemists are engaged in unravelling the 'mysteries' associated with life including *genetics* and aging. When man's rate of aging is slowed down,...!

1.4 LANDMARKS IN CHEMICAL SCIENCE

Prior to the systematic development of chemical science from the second half of the 18th century, various discoveries had been made which are significant for understanding modern chemistry. These include processing of various metals and alloys, manufacture of special materials like glass, special chemicals like sulphuric acid, etc. In addition, important advances had been made in the allied sciences of physics and biology. However, we summarise below some of the major milestones in the progress of chemical science (defined in the broadest sense) after it emerged as a systematic science in the second half of the 18th century. [The names with asterisks in the list are the Nobel prize winners (not necessarily in chemistry).]

1750   Discovery of oxygen (Priestley, Scheele)
        Discovery of electrostatic interaction (Coulomb)
        Reversal of phlogiston theory (Lavoisier)
        Birth of quantitative chemistry (Lavoisier)
        Study of current electricity (Galvani, Volta, Ampere)
        Discovery of rotary engine (Watt) and wrought iron (Cort)

1800   The atomic theory (Dalton)
        Avogadro's hypothesis (Avogadro)
        Advances in inorganic chemistry (Berzelius)
        First modern textbook of chemistry (Berzelius)
        Laws of electromagnetism (Oersted and Faraday)
        Second law of thermodynamics (Carnot)
        Beginning of electrochemistry (Davy and Faraday)

Birth of organic chemistry (Woehler, Dumas, Liebig, Pasteur, Kekule and vant H, ff*)

The cell theory (Schleiden and Schwann)

1850   Conservation of energy (Meyer, Joule, Helmholtz)

Development of kinetic theory (Bernoulli, Clausius, Maxwell)

Determination of atomic masses (Cannizaro)

Production of cast steel (Bessemer)

The electromagnetic theory of light (Maxwell)

The periodic table (Mendeleev)

Theory of electrolytic dissociation (Arrhenius*)

Theory of evolution (Darwin)

Germ theory of disease (Pasteur)

Discovery of DNA (Miescher)

Open hearth process (Siemen)

Thermodynamics systematised (Gibbs)

Statistical thermodynamics (Boltzmann, Gibbs)

Discovery of electric light (Edison) and radio waves (Hertz*)

Discovery of inert gases (Ramsay*, Raleigh*)

Manufacture of dyes and explosives

Principles of chemical equilibrium (vant Hoff*, Ostwald*)

Discovery of cathode rays (Crookes), and positive rays (Lenard*)

Measurements of increased precision on mechanical properties of materials

Tetrahedral carbon atom (vant Hoff*, Le Bel)

Synthesis of dyes (Perkin)

Rise of biochemistry (E Fischer*, Kossel*)

Discovery of X-rays (Rontgen*)

Enzymes (Büchner*)

Vitamins (Eijkman*)

Study of radioactivity (Becquerel*)

1900   Rediscovery of Mendel's laws of genetics (Correns, Tschermaks de Vries)

Photosynthesis (Willstatter*)

Isolation of the first hormone: Epinephrine (Takamine, Aldrich)

Quantum theory (Planck*)

Nernst heat theorem: Third law of thermodynamics (Nernst*)

Isolation of radium and polonium (Curie*)

Radioactive transformations (Rutherford* and Soddy*)

Mass and charge of the electron (Thomson*, Millikan*)

Special theory of relativity (Einstein*)

Photoelectric effect (Einstein*)

Organic drugs (Baeyer*)

Beginning of chemotherapy (Ehrlich*)

1910   The mass spectrograph (Aston*)

X-ray diffraction (Laue*, Bragg*)

Reliable atomic masses (Richards*)

Birth of coordination chemistry (Werner*)

Reactions in organic chemistry (Grignard*, Sabatier*)

Synthesis of ammonia (Haber*)
Nuclear model of the atom (Rutherford* and Bohr*)
X-ray spectra (Moseley)
Theories of valency (Kossel*, Lewis, Langmuir*)

1920 First nuclear disintegration (Rutherford* and Soddy*)
Ultracentrifuge (Svedberg*)
Radio broadcasting (Marconi* and Braun*)
Quantum mechanics (de Broglie*, Heisenberg*, Schrödinger*, Dirac*)
Exclusion principle (Pauli*)
Hormones: Insulin (Banting*)
Discovery of cosmic rays
Theory of strong electrolytes (Debye* and Hückel)
Electrolytic conduction (Onsager*)
Birth of polymer chemistry (Staudinger*)
Explanation of covalent bond (Heitler, London)
Raman effect (Raman*)
Isolation of the first vitamin: Thiamine (Jansen and Donath)
Cellulose, plastics and rayon were developed
Synthesis of petrol from coal (Fischer, Tropsch, Bergius*)
Discovery of labile phosphate—ATP (Lohmann: Fiske and Subbarow)
Theory of metal (Sommerfeld, Pauli*, Bloch*)
Crystal field theory (Bethe*)

1930 Electron theory (Dirac*)
Development of quantum chemistry (Pauling*, Mulliken*, Slater Hund, Coulson, Eyring)
Discovery of neutron (Chadwick*)
Reciprocity relations (Onsager*)
Study of artificial radioactivity (Joliot*)
Crystalline enzymes (Sumner*, Northrop* and Stanley*)
Vitamin D (Windaus*)
Vitamin C (St. Gyorgyi*)
Chromosomes and theory of heredity (Morgen*)
Geochemistry (Goldschmidt)
Meson theory (Yukawa*)
Positive electron and meson (Anderson*)
Structure of fibres
Plasticity of metals
Cytochrome (Keilin)
TCA cycle (Krebs*)
Antibiotics—penicillin (Fleming*, Florey*, Chain*)
              —sulphonomides (Domagk*)
Electric nature of nerve impulse (Adrian* and Sherrington*)
Nuclear origin of sun's heat (Bethe*)
Development of radar
Dislocations in crystals (Taylor)
Liquid drop theory of nucleus (Bohr*, Wheeler)
Nuclear fission (Hahn*)

Servo-mechanism and electronic computers
Development of jet planes and rockets
Phenomena of metal plasticity (Orowan)
Polymerisation
Artificial rubber
Reaction rate theory (Wigner*, Eyring, Polanyi)

1940 X-ray studies of crystalline proteins (Perutz*)
Large-scale manufacture of penicillin
Electron microscope
Discovery of actin and actomysin (Szent-Gyorgyi*)
Meson field theory (Yukawa*)
Cybernetics (von Neumann, Wiener)
One gene–one enzyme relationship (Beadle* and Tatum*)
Nylon and many varieties of new plastics
Shell theory of nucleus (Goppert, Mayer*, Jensen*)
Atomic bomb
Role of ATP in the energy-transfer cycle (Lipmann*)
Paper chromatography (Martin*, Synge*)
Amino acid sequence in proteins (Sanger*)
Electron microscope studies of virus and bacteriophage
Cortisone, Vitamin B-12
Quantum electrodynamics (Schwinger*, Feynman*, Tomonoga*)
Cosmic ray disintegrations
Organic synthesis and reaction mechanisms (Robinson*, Ingold)
Diels*–Alder* reactions
Progress in polymer chemistry (Flory*)
Radio astronomy
Nuclear magnetic resonance (Bloch* and Purcell*)
Dislocation theory of plasticity and growth of crystals (Mott, Franc, Read)
Use of tracer elements in chemistry

1950 Thermonuclear reaction
Conformation and chemical reactivity (Barton*, Hassel*)
Transistors (Bardeen*, Shockley* and Brattain*)
Progress in irreversible thermodynamics (Prigogine*)
Synchrotron, transuranium elements (McMillan*, Seaborg*)
Application of crystal field theory to inorganic chemistry (Hartmann, Orgel)
Development of semi-empirical quantum mechanical theory for molecules (Pople, Parr)
X-ray analysis of protein structures (Pauling* and Corey)
Stereoregular polymers (Zeigler* and Natta*)
Photoflash spectroscopy (Eigen*, Porter* and Norrish*)
Synthetic ACTH
Commercially available analytical instruments in chemistry
Mechanised surgery (Gudov, Androsov)
Chemical changes in nerve (Hodgkin*)
Anti-proton, neutrino

Cerenkov effect (Cerenkov*)
Genes and heredity (Beadle*, Tatum* and Lederberg*)
Automation, computers
Kinetics of chemical reactions (Semenov* and Hinshelwood*)
Mossbauer effect (Mössbauer*)
Multiplication of elementary particles
Theory of superconductivity (Bardeen*, Cooper* and Schreifer*)
Elucidation of photosynthesis (Calvin*)
Analysis of brain currents (Grey Walter)
Non-conservation of parity (Lee*, Yang*)
Molecular biology—structure of nucleic acids
    (Watson* and Crick*, Wilkins*)
Autoradiography of cells
Electron microscopic study of cell organelles
Crystal structures of biological molecules (Kendrew*, Perutz*,
    Phillips, Hodgkin*, Pauling*)

1960   Laser
Maser (Townes*, Basov* and Prochorov*)
Sera for poliomyelitis
Radioimmunoassay (Yallow*)
Quantum organic chemistry
Progress in *ab initio* calculations
Synthesis of inert gas compounds (Bartlett)
Chemiosmotic hypothesis (Mitchell*)
Automation of protein synthesis
Vitamin B-12 synthesis (Woodward*)
Elucidation of the genetic code (Nirenberg*, Ochoa*, Khorana*)
Synthesis of a gene (Khorana*)
Structure of transfer RNA (Holley*)
Photoelectron spectroscopy (Siegbahn, Turner)
Regulatory processes in biochemistry (Jacob*, Monod*, Changeaux,
    Wyman, Koshland)
Isolation of a single gene (Beckwith)
Cyclic AMP as chemical messengers (Sutherland*)
Molecular biology of antibodies (Edelman* and Porter*)
Role of orbital symmetry in chemical reactions
Woodward–Hoffman rules (Woodward* and Hoffman)

1970   Affinity chromatography (Cuateseasas)
Restriction endonuclease (Arbor, Nathans, Smith)
Nucleotide sequence analysis (Sanger* and associates)
Reverse transcriptase and its implication in tumor development
    (Baltimore and Temin)
Gene cloning (Cohen)
Split genes (Chambon, Leder)

The chemists are a strange class of mortals who seek their pleasures among soot and flame,
poisons and poverty, yet among all these evils I seem to live so sweetly that may I die if I
would change places with the Persian king.

JOHN JOACHIM BECHER (1625–82)
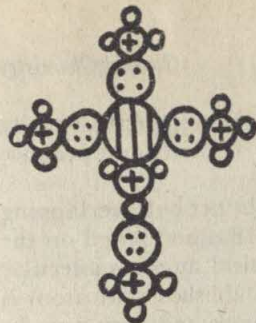
2

Classical Atomic-
Molecular Theory[*]

If, in some cataclysm, all of scientific knowledge were to be destroyed and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis . . . that all things are made of atoms. . . . In that one sentence . . . there is an enormous amount of information about the world, if just a little imagination and thinking are applied.

RICHARD FEYNMAN

The science of chemistry is primarily concerned with the structure, energetics, and transformations of material substances. Matter occurs in nature in bewildering variety. Some prominent examples include air, water and earth; stones, rocks and mountains; satellites, planets and galaxies; plants, animals and man; and food, shelter and clothing. The list is endless. All these substances exhibit a myriad of shapes, sizes, colours, odours and other properties. However, chemists have found that underneath this infinitely diverse appearance and behaviour, there is considerable conceptual unity and it will be our attempt in this and the following two chapters to introduce those principles that provide the basis for understanding the properties and behaviour of substances.

Amongst the various theories of matter, the most fundamental is the atomic-moleculr theory. The triumph of the atomic-molecular approach lies in its ability to rationalise and correlate most of the macroscopic properties of matter by invoking a few microscopic concepts.[†] Thus, it is now established that the nature of atoms and molecules controls chemical (e.g. reactivity). physical (e.g. density), mechanical (e.g. rigidity), optical (e.g. colour), thermal, electrical, magnetic and other properties.[‡] In short, the atomic-

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[*] We use the term 'classical' to refer to that part of the atomic-molecular theory which is based on the structureless atom. The extension of this theory, based on the electronic structure of the atom, will be called modern atomic-molecular theory.

[†] The terms 'macroscopic', 'microscopic' and 'concept' are explained in Chapter 1.

[‡] Two common properties, taste and odour, do not have a satisfactory atomic-molecular explanation as yet. For example, we do not understand why salt is 'salty' or sugar is sweet.

17

molecular theory exposes the underlying unity behind the apparent diversity of matter and it, therefore, systematises and simplifies the study and practice of chemistry.

The atomic-molecular theory has developed in two distinct but overlapping phases. The first phase started by John Dalton around 1804 and based on the concept of the indivisible atom, may be called the classical atomic-molecular theory. About the turn of this century, experiments established that atom is not indivisible; rather, it is composed of electrons, protons and neutrons. In the second phase, which may be termed as the modern atomic-molecular theory, it is the electron, and not the atom, which plays the central role. The modern approach has not invalidated all the classical ideas; it has only made them more comprehensible.

This chapter gives an account of the main ideas of the classical atomic-molecular theory. After a brief review of the pre-scientific notions of matter, we shall examine the broad classifications of matter based on macroscopic behaviour followed by the so-called laws of chemical combination. These laws provided the impetus for the assumption that indestructible atoms are the ultimate building blocks of all matter. Then following a statement of Dalton's postulates about the nature of atoms, we show how these postulates, when combined with some experimental measurements, led to the concept of molecules as well as of molecular formulae and also enabled the determination of relative atomic masses. The molecular formulae suggested the idea of chemical equations which is an elegant way of expressing the qualitative and quantitative features of a chemical reaction. We conclude this chapter by discussing how the relative atomic mass scale and molecular formulae contributed to two of the most important ideas in chemistry—namely the periodic table and the concept of molecular structure.

2.1 ANCIENT SPECULATIONS ON THE NATURE OF MATTER

Speculation about the nature of something as omnipresent as matter dates back to very ancient times. As early as 500–600 B.C. it was suggested by several philosophers that there are two categories of matter—one consisting of primary substances called the elements and the other consisting of rest of substances formed by the combination of the elements. These thinkers also proposed that air, water, earth, and fire were the four elements from which the entire universe was made. This may be called a macroscopic description. The microscopic viewpoint put forward by Indian* and Greek philosophers

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*It is not generally appreciated that Indians proposed the atomic hypothesis before the Greeks. 'Indian atomism was certainly independent of Greek influence, for an atmoic theory was taught by *Pakudha Katyayama*, a contemporary of Buddha, and was therefore earlier than that of Democritus. The Vaisesika school, which specially elaborated atomic doctrines, maintained that before combining to form material objects, atoms made primary combinations of diads and triads. This doctrine of molecules was developed differently by Buddhists who taught that in normal conditions no atoms existed in a pure state, but only combined in different proportions in a molecule (*Samghata, Kalapa*). The atomic theories of ancient India are brilliant imaginative explanations of the physical structure of the world; though it is probably mere coincidence that they agree in part with the theories of modern physics, they are nevertheless much to the credit of the intellect and imagination of early Indian thinkers.' (From A. L. Basham *The Wonder that was India*, Sidgwick and Jackson, London, 1967.)

held that matter was made of invisible and indivisible atoms. However, these speculations proved sterile for further development since no link was established between the concepts and the observable and measurable behaviour of matter. As such, none of the assertions made could either be proved or disproved. The ancient philosophers used only logic and intuition but no experiments to attack a problem and these were insufficient to explore natural phenomena.

2.2 RISE OF CHEMICAL SCIENCE

The scientific method emerged in the 16th century with the realisation that investigation must supplement logic and intuition in probing nature. This viewpoint, which owes its initiation to scientists like Bacon, Boyle, Galileo, Hooke, Newton and others, recorded its early successes in astronomy and mechanics. The method came to be gradually applied to chemical behaviour of matter, thanks to the pioneering effort of Antoine Lavoisier in the late 18th century and this marked the birth of chemical science as we know today.

2.2.1 Classification of Matter

The study of matter is facilitated by adopting some scheme of classification which brings some order into its otherwise complex behaviour. Two general schemes have been found useful in chemistry which we now describe.

Every material substance can be characterised by a large number of properties like size, shape, texture, colour, mass, melting and boiling points, reactivity and so on. Observation of some of these properties reveals interesting regularity. Thus, on the basis of rigidity, volume, and shape, it is possible to separate all matter into three categories: solid, liquid and gaseous. A solid is rigid, occupies definite volume and possesses definite shape. A liquid is not rigid (i.e. it flows), but it has definite volume. A liquid has no intrinsic shape; it assumes the shape of the container. A gas has no rigidity, intrinsic shape, or intrinsic volume; the shape and volume of the container is the shape and volume of the gas. Solid, liquid and gas are referred to as the states of aggregation and they form the basis of the physical classification of matter.* A fourth state of aggregation called plasma consists of charged particles and it exists only at very high temperatures. This state is not encountered under ordinary terrestrial conditions.

The chemical classification depends on the fact that material substances are either pure, in the sense that they have a definite and invariant composition; or mixtures, in the sense that they contain two or more pure substances mixed together. Properties of a mixture vary as the composition of the mixture is varied. For example, density, refractive index, boiling point, etc., of a mixture of salt and water change as the concentration of salt is changed. Mixtures are said to be homogeneous if the composition is the same throughout the sample (e.g. sugar and water), or heterogeneous if the composition is different in different parts of the mixture (e.g. salt and sand).

Substances present in a mixture will always have one or more different properties which can be used to separate the mixture into pure substances. Examples of some common methods

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*There are some substances (e.g. liquid crystals) which do not fit into one or the other states of aggregation.

of separation are distillation (based on difference in boiling points), crystallisation (difference in solubilities) and chromatography (difference in distribution between a stationary and a moving phase) while examples of some less common methods are ultra-centrifugation (difference in sedimentation velocity in a centrifugal field) and electrophoresis (difference in electrical mobility).

The study of chemical behaviour shows that pure substances are of two types —*elements and compounds*. A compound is one which on transformation yields simpler substances while an element cannot be converted into anything simpler by any means. How can one decide whether a substance is ' simple ' or not? Lavoisier and other early chemists answered this question by choosing the experimentally measurable property of mass as the criterion of simplicity. For example, it is found that 1 g of mercuric oxide on heating produces 0·926 g of mercury and 0·074 g of oxygen. This shows that mercuric oxide cannot be an element since it decomposes to give mercury and oxygen which have smaller masses. Thus, if a substance cannot be converted by any process into products having smaller mass, the substance was considered to be an *element*.* One can legitimately ask, ' What guarantee is there that a substance regarded as an element today may not be broken down in future by as yet, unknown process?' The historical answer† to this question was again given by Lavoisier: ' We cannot be sure that what we now regard as an element is in fact one—all we can say is that such a substance is the present limit of chemical analysis and cannot be split up further so far as we know at present'. In the developing stages of chemistry confusion arose frequently, but repeated experimentation under different conditions established the list of elements on increasingly firmer footing.‡ At present, 105 elements have been identified of which ninety-two occur in nature while the remaining are man-made (in the laboratory). The physical and the chemical classification of matter is summarised in Chart 2.1. (All the known elements are listed on the inside cover of the book.)

2.2.2 Laws of Chemical Combination: A Summary of Macroscopic Behaviour in Chemical Reactions

The laws of chemical combination played an important role in the formulation of the atomic-molecular theory. These laws summarise the experimental results that are obtained about the masses of the reactants and products in a very large number of chemical reactions. The various laws are:

(*i*) *Law of conservation of mass* which states that the total mass of the reactants is equal to the total mass of the products in every chemical reaction. In other words, a chemical reaction is merely transformation of material substances; it involves neither creation nor destruction of mass. (See, for example, the decomposition data of mercuric oxide given above.)

*This is an illustration of an operational definition of a scientific concept which means defining a concept in terms of a procedure which can be experimentally observed and measured (see Chapter 1). The ancient concept of an element was not operational since it did not specify how to decide whether a substance was an element or not on the basis of experiment.

†The modern answer is based on the concept of atomic number discussed in Chapter 3, section 3.2.

‡A good example is lime which was taken as an element until it was discovered that it decomposes at very high temperatures.

Chart 2·1 Classification of Matter

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                    ┌─────────────┐
                    │ The Universe │
                    └─────────────┘
                 ┌──────────┴──────────┐
            ┌────────┐            ┌───────────┐
            │ Matter │            │ Radiation │
            └────────┘            └───────────┘
        ┌───────┴────────┐
   Physical          Chemical        (For classification of radia-
   Classification     Classification  tion see Table 3·1).

 ┌────────────────────┐   ┌─────────────────────┐
 │ Solids, Liquids, Gases │ │ Elements, Compounds, │
 └────────────────────┘   │      Mixtures         │
                          └─────────────────────┘
              Classified
              according to the
              periodic table

                          Inorganic        Organic
                          compounds        compounds
```
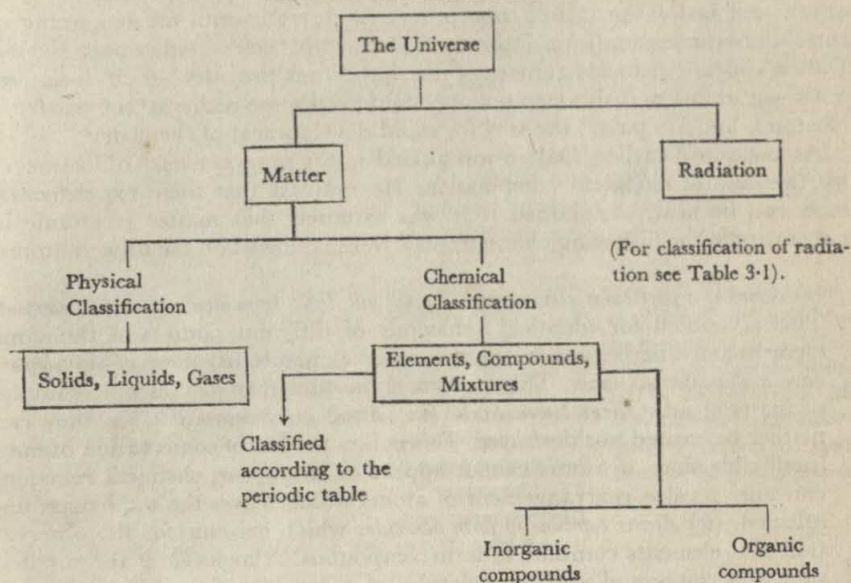
(*ii*) *Law of definite proportions* which states that every compound always consists of the same elements present together in a fixed proportion by mass. For example, 9 g of water, irrespective of source and method of preparation of the sample, always yields 1 g of hydrogen and 8 g of oxygen.*

(*iii*) *Law of multiple proportions* which states that whenever two elements combine to form two or more compounds, the masses of one of the elements that combine with a fixed mass of the other element are in a ratio of small integral numbers. This law may be illustrated by considering the compounds water and hydrogen peroxide both of which contain the elements hydrogen and oxygen. Now, water yields hydrogen and oxygen in the mass ratio of 1:8, while in hydrogen peroxide the mass ratio is found to be 1:16. Therefore, the amount of oxygen in the two cases that combines with a fixed amount of hydrogen is 8:16, or 1:2, which is a ratio of small integers.

2·3 THE ATOMIC THEORY OF JOHN DALTON

At the time when the macroscopic classification of matter was being developed, scientists were also wondering about the microscopic nature of material substances. The idea that matter is discrete and consists of atoms was by far the most popular view. For instance, particulate character was implicit in the laws of motion, enunciated by Issac Newton, which so successfully described the dynamics of material bodies in space and time. Similarly, the model of a gas which later formed the basis of the kinetic theory of gases also assumed the atomic nature of matter. None of these theories, however,

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*The *Law of definite proportions* is rigorously valid for compounds containing molecules as discrete units. When either atoms or ions are discrete units, the law need not be necessarily valid. Compounds which do not obey the law are called *non-stoichiometric compounds*. See Chapter 7 for further details.

provided any information about any property (e.g. size, shape, mass, etc.) of atoms and hence the atomic concept remained vague until the beginning of the 19th century when John Dalton put forward his celebrated atomic theory. Dalton's ideas led to assignment of one important property—their (relative) mass—to atoms and this step not only conferred some reality to the existence of atoms, but also paved the way for rapid development of chemistry.

As mentioned earlier, Dalton was guided to the main concepts of his theory by the laws of chemical combination. He realised that these experimental facts can be neatly explained if it was assumed that matter is atomic in nature and if the following characteristics were endowed on the unseen atoms:

(*i*) *Atoms of a particular element are all alike but differ from atoms of another element.* This accounted for identical behaviour of different samples of the same element and different behaviour of different elements. (*ii*) *Atoms of each element have a characteristic mass.* This explained the fact that macroscopic samples of material substances have mass. (*iii*) *Atoms are indestructible*, i.e. they can neither be created nor destroyed. This makes the law of conservation of mass intelligible since if atoms cannot appear or disappear, chemical reactions can only involve rearrangement of atoms which leaves the total mass unaffected. (*iv*) *Atoms combine to form molecules* which accounts for the observation that elements combine to form compounds. A molecule is the smallest unit of a compound and all molecules of a compound are identical, each molecule containing a fixed number of atoms of the constituent elements. This assumption about atomic behaviour explains the law of definite proportion as well as the law of multiple proportion as shown in Figs. 2.1, 2.2 and 2.3.*

These four statements, known as the postulates of Dalton's atomic theory, nicely illustrate the strength and limitations of speculation in scientific theory. The mass relationships expressed in the laws of chemical combination are hard facts; they can be verified experimentally by anyone. As factual statements, they are but useful summaries and no more. The strength of a theory is that it tries to extract more information from raw facts by speculation—it provides the rational basis for predictions. Speculations and predictions in science are not a result of fancy imagination—they have to be consistent with observations and measurements performed in the laboratory. A good theory also suggests lines for further development which provide further checks on the validity of its speculative concepts. A theory may become untenable in parts or in totality on further experimentation. It has then to be modified or replaced by another more comprehensive theory. Thus, though atoms cannot be seen directly, their existence is consistent with facts. The assumption of their existence suggested a whole range of new ideas which on testing were found to be generally correct. The assumption of indestructibility of the atom, however, was refuted experimentally and therefore modern atomic theory starts from the structure of the atom. The constant interaction between theory and experiment is the crux of the scientific method and the student should realise that chemistry is not experiment *versus* theory, but experiment *and* theory.

*We have deviated from historical order in (*iv*). Dalton proposed the atomic theory on the basis of the laws of conservation of mass and of definite proportions. He then showed that the law of multiple proportions, unknown at that time, is a logical consequence of his theory. Experimental verification soon followed, thus lending credibility to Dalton's views. Also, the concept of molecule was not clearly formulated by Dalton, but was later developed by Avogadro.
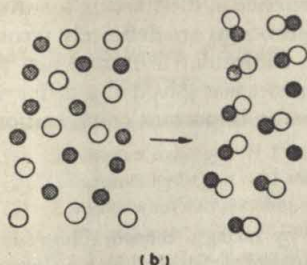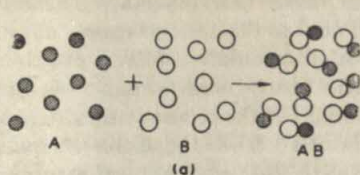
Fig. 2.1 An atomic view of the law of definite proportion. (a) The combination of atoms of element A with atoms of element B to form molecules of the compound AB, if equal number of A and B atoms are present. (b) The same reaction as in (a) but for unequal number of atoms. There are twelve atoms of A but only ten atoms of B; hence two atoms of A are left over. (a) and (b) together show that the compound AB always contains a fixed composition of elements A and B. In this case the ratio is 1 : 1.
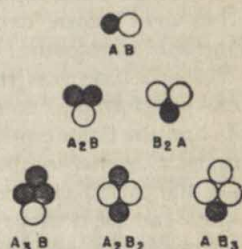
Fig. 2.2 The combination of A and B need not always be in the ratio 1 : 1. However, since atoms are assumed to be indivisible, the combination must involve integral numbers of atom. Some of the possibilities are shown here.
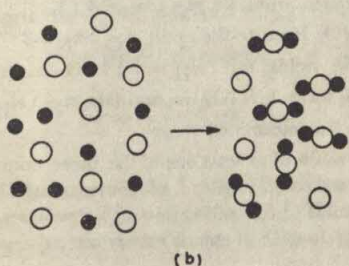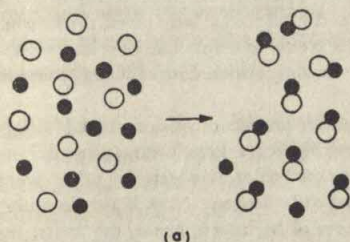
Fig. 2.3 An atomic view of the law of multiple proportion: (a) Combination of elements A and B to form compound AB in which the atomic ratio is 1:1. (b) Another combination of the same elements to form compound A_2B in which the atomic ratio is 2:1. In A_2B there are twice as many atoms of A which combine with one atom of B. Therefore, it follows that the mass of A that combines with a fixed mass of B in A_2B and AB should be in the ratio 2 : 1. The same type of argument when used for other combinations of A and B, shows that the ratio is always expressible as small integers.

2.4 THE PROBLEM OF RELATIVE ATOMIC MASSES AND OF MOLECULAR FORMULAE

The immediate question raised by the atomic theory was: 'If an atom has mass how can the mass be experimentally determined?' Dalton recognised that there was no way available to him to determine the absolute masses of atoms of various elements. Relative *atomic masses* could, however, be obtained from decomposition data on compounds, if the formulae (i.e. number and types of

atoms) of the compounds were known. On the other hand, if relative atomic masses were known, experimental data would enable the determination of the formula of a compound (see section 2.4.7 for such calculations). The problem at Dalton's time was that neither was known. Thus, there existed a vicious circle—the formulae could not be determined without the relative atomic mass scale and the latter could not be obtained without a knowledge of the *molecular formulae*. One way to break this vicious circle was to start with a set of assumed molecular formulae. From this the atomic masses can be worked out, which in turn can yield more molecular formulae. If in a large number of cases, no inconsistency is observed, then it provides confidence in the starting assumptions; if inconsistency is detected, the starting assumptions are definitely wrong and then different initial assumptions about the molecular formulae are required. Historically, the riddle of relative atomic masses was solved in a different way by Cannizzaro who based his considerations on important contributions made earlier by Gay-Lussac and Avogadro.

2.4.1 Dalton's Unsuccessful Attempt

The statements made above will perhaps become clearer by taking a concrete illustration. Dalton attacked the problem by assuming that (*a*) all elements are monatomic, (*b*) the simplest combination of elements involves joining together of individual atoms, and (*c*) the most common binary compound of two elements represents the simplest combination of those two elements. Thus, the elements hydrogen, oxygen and nitrogen were written as H, O and N respectively, where the symbols stand for single atoms of these species. Further, the three common binary compounds of these elements namely water, ammonia and nitric oxide were given the formulae OH, NH and NO respectively. With these assumptions, it is easy to determine the relative masses of an atom of hydrogen, oxygen and nitrogen from the decomposition data of water, ammonia and nitric oxide.

Experimental analysis of water shows that 100 g of water on decomposition yield 11·19 g of hydrogen and 88·81 g of oxygen. Therefore, hydrogen contributes 11·19 per cent to the total mass of water and oxygen contributes 88·81 per cent to the total mass of water. In other words, oxygen contributes $(88·81/11·19) \approx 8$ times as much mass as hydrogen. Now, if the formula of water is OH, then there is one oxygen atom for each atom of hydrogen, hence, the mass, m_O, of oxygen atom is eight times the mass, m_H, of the hydrogen atom, i.e. $m_O : m_H = 8 : 1$.

Similar reasoning for nitric oxide (assumed formula NO) leads to the result, $m_O : m_N = 8 : 7$, which when combined with the oxygen : hydrogen ratio yields, $m_N : m_H = 7 : 1$. However, if we analyse the ammonia data on the assumption that its formula is NH, we find that $m_N : m_H = (14/3) : 1$ which differs from the hydrogen–nitrogen ratio determined above.

This discussion clearly shows that the choice of the formula of at least one of the three compounds, namely water, ammonia, or nitric oxide, must be wrong. One can, of course, start all over again and go on making various choices for the formulae until a self-consistent* *atomic mass scale* is obtained. However, as mentioned earlier, the determination of atomic masses was achieved by an entirely different method.

2.4.2 Gay-Lussac's Law and Avogadro's Hypothesis

Gay-Lussac, during a study of chemical reactions in the gaseous phase, found that the volumes of the reactants and products in a large number of chemical reactions are related to each other by small integers, provided the volumes are measured at a common temperature and pressure. For example, in the

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*The term self-consistent here means, a set of formulae and a set of atomic masses which are consistent with each other, i.e. they do not lead to contradictions.

reaction of hydrogen gas with oxygen gas to produce water vapour, it was found that, two volumes of hydrogen and one volume of oxygen will give two volumes of water vapour. The results for a few other reactions are summarised in Table 2.1. Gay-Lussac's discovery of integer ratios in volume relationships is actually the law of definite proportions *by volume*; the law of definite proportions stated earlier being with respect to *mass*.

The occurrence of integers in volume relationship as well as in mass relationship led Avogadro to make the brilliant suggestion that *equal volumes of all gases under identical conditions of pressure and temperature, contain equal number of particles.** This assumption commonly known as *Avogadro's hypothesis*, when

Table 2·1 Summary of Volume Relationships in a number of Reactions between Gaseous Substances

(1)	2 volumes hydrogen + 1 volume oxygen	→ 2 volumes water vapour
(2)	3 volumes hydrogen + 1 volume nitrogen	→ 2 volumes ammonia
(3)	2 volumes sulphur dioxide + 1 volume oxygen	→ sulphurtrioxide (solid)
(4)	1 volume ammonia + 1 volume hydrogen chloride	→ ammonium chloride (solid)
(5)	2 volumes carbon monoxide + 1 volume oxygen	→ 2 volumes carbon dioxide
(6)	1 volume nitrogen + 1 volume oxygen	→ 2 volumes nitric oxide
(7)	1 volume oxygen + carbon (solid)	→ 2 volumes carbon monoxide

combined with the assumption of the indivisible atom, leads to the formulae of elementary gases like hydrogen, oxygen, chlorine, etc., as the following discussion illustrates.

2.4.3 Concept of a Molecule, Formulae of Elementary Gases and Atomic Masses of Hydrogen, Oxygen and Nitrogen

The volume relationship observed in the reaction of hydrogen and oxygen to produce water vapour can now be rewritten. Since all the volumes have been measured at constant temperature and pressure, equal volumes should contain equal number of particles. If unit volume has n particles then

n particles of oxygen + $2n$ particles of hydrogen → $2n$ particles of water vapour

or 1 particle of oxygen + 2 particles of hydrogen → 2 particles of water vapour

This means that 1 particle of water contains 1/2 particle of oxygen but since an atom cannot be subdivided (by assumption) it follows that a particle of oxygen cannot be a single atom. Therefore, a particle of oxygen must contain an even

*Avogadro's statement seems ridiculous at first glance since experience shows that a fixed-volume container does not contain equal number of different objects. For example, a box does not hold as many potatoes as peas. The statement appears more plausible when it is realised that particles of a gas are not in contact (as peas and potatoes are in a box), which means that absolute volumes (unlike masses) of the gas particles have little significance. Of course, plausibility of a statement does not constitute a proof; the proof of Avogadro's hypothesis came only after the kinetic theory model of gases was developed (see Chapter 6). Until then, Avogadro's conjecture was used mainly because it enabled the determination of a consistent relative atomic mass scale.

number of atoms. (Odd number of atoms would imply a subdivision of an atom.) A particle which is made up of a group of atoms was named *molecule* and our analysis leads to the conclusion that the oxygen molecule is not monatomic as Dalton had assumed. Of course, the analysis does not decide how many even number of atoms should be in the oxygen molecule but here the simplest possibility, namely diatomic, was tried and it turned out to be the correct one.*

The volume data of the hydrogen–chlorine reaction led in a similar fashion to the conclusion that the hydrogen molecule is diatomic. Based on this, the volume relationship of the hydrogen–oxygen reaction can be interpreted as:

1 molecule of oxygen + 2 molecules of hydrogen→ 2 molecules of
water vapour

That is,

$$O_2 + 2H_2 \longrightarrow \text{2 molecules of water}$$
$$\text{or } \tfrac{1}{2}O_2 + H_2 \longrightarrow \text{1 molecule of water}$$
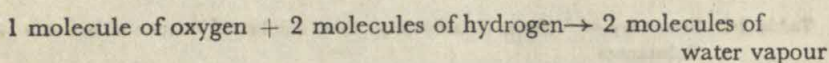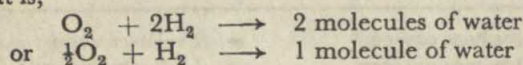
Therefore, the formula of water must be H_2O.

In the same manner, the formula of ammonia was established as NH_3. From these formulae and the decomposition data of ammonia and water given earlier, it can be verified that the relative atomic masses of hydrogen, oxygen and nitrogen are nearly in the ratio of $1:16:14$. These values do not lead to contradiction for other compounds and hence were assumed to be correct.

2.4.4 The Atomic Mass Unit (amu) Scale

In the analysis given above, an atomic mass of 1 was assigned to an atom of hydrogen because hydrogen is the lightest element known. This choice was made by Dalton also. Relative to this mass, the exact mass of an oxygen atom turns out to be 15·88. Later it was found that if an oxygen atom was taken as the reference and assigned a value of 16·000, then the atomic masses of most other elements will be whole numbers or close to whole numbers. Because of this convenience, oxygen became the accepted standard. The ratio of the mass of any atom to 1/16 of the mass of oxygen atom is the relative atomic mass (or simply atomic mass) of that element and these masses are said to be in the *atomic mass unit* (amu). On the scale in which the oxygen atom mass is 16·000 amu, hydrogen atom mass is 1·008 amu. It is obvious that the mass of a molecule should be equal to the sum of the masses of the constituent atoms. Thus, molecular masses can be expressed in amu, if the atomic masses and the formulae of the molecules are known.

It is important to appreciate fully the nature of the arbitrary choice of a reference. The necessity of a reference arose because initially there were no methods to experimentally determine the mass of individual atoms. The mass of a single atom can be determined only if a large number of atoms can be weighed and at the same time counted as well. Experimental methods for counting atoms were discovered much later and in their absence, the 19th century chemistry had to choose a standard in an arbitrary manner. The masses in the amu scale are dimensionless numbers having only relative, but not absolute, significance.

*The diatomic nature of oxygen, hydrogen, chlorine, etc., is now confirmed by several independent evidences.

2.4.5 The Mole Concept

We now introduce the important concept of *mole* which plays a key role in chemical calculations. The need for this concept arises because the basic unit in chemistry is an atom or a molecule. Therefore, a way has to be found which permits a chemist to take a definite number of atoms or molecules while dealing with macroscopic samples of matter. Just as a dozen (twelve objects), a score (twenty objects), and many other units have been invented to facilitate counting of objects like nails, bananas, etc., a *mole* is the chemist's unit for counting atoms, molecules, ions and other microscopic species.* A mole means a collection of 6.02×10^{23} objects; whereas a dozen or a score is defined in terms of a number, a mole was originally defined in terms of mass (and only indirectly in terms of a number). There are two reasons for this difference. Firstly, when the mole concept was introduced there were no experimental methods available for counting atoms or molecules and secondly, even when these methods became available, the direct counting of atoms in a macroscopic sample is not practical.†

Let us now examine the logic underlying the original definition of a mole in terms of mass. As has been shown, the mass of a hydrogen molecule (H_2) is 2·02 and the mass of an oxygen molecule (O_2) is 32·00 in the amu scale (with O atom $= 16.00$ as the reference). Since all atoms of an element and all molecules of a compound are assumed to be identical, the mass ratio of a particular number of hydrogen molecules and the same number of oxygen molecules will also be 2·02 : 32·00. Conversely, if two samples, one containing hydrogen gas and the other oxygen gas, have a mass ratio 2·02:32·00, then the first sample must contain as many hydrogen molecules as the second sample contains oxygen molecules. In particular, if there are N_0 molecules in 2·02 g of hydrogen gas, then there must be N_0 molecules in 32·00 g of oxygen gas. By the same reasoning, the number of grams of any compound (or element) equal to its molecular (or atomic) mass must also contain N_0 molecules (or atoms). This characteristic number N_0 is called the *Avogadro number* and the mass in grams of any compound (or element) that is numerically equal to its molecular (or atomic) mass in amu is called a mole. Our argument does not fix the value of N_0, but provides a way of picking the relative number of atoms and molecules without resorting to direct count. Much later, when methods for counting atoms and molecules developed, the value of the Avagadro number N_0 could be determined and it is a triumph of atomic-molecular theory that several independent methods yield identical value of N_0, namely 6.02×10^{23}. The use of the mole concept in chemical calculations will be illustrated with several examples later in this chapter.

The choice of gram as the unit of mass in the definition of a mole is, of course, entirely arbitrary. One could have equally well chosen ounce, pound or ton. Gram was chosen because it is the most commonly used unit in chemical laboratory. To emphasise this point, the above definition of a mole is sometimes referred to as gram-mole. Similarly, an ounce-mole, or a pound-mole can also be defined. Since there are 6.02×10^{23} particles in a gram-mole, it follows that there must be $453 \times 6.02 \times 10^{23}$ particles in a pound-mole (1 pound$=453$ g).

The fact that a mole is related to the number of particles means that it must be also related to volume of all gases because equal volumes of all gases

*We use the symbol mol to represent mole.

†At the rate of one second per count, it will take 10^{16} years to count a mole of objects!

under the same condition of pressure and temperature contain equal number of particles. This is indeed supported by experiment. Thus it is found that at a pressure of 760 mm of Hg and 100°C, one mole of all gases occupies 22·4 litres of volume. This particular choice of pressure and temperature is again arbitrary; it has been done for convenience only. The pressure of 760 mm of Hg and temperature of 0°C are called standard pressure and temperature (STP). To summarise, 22·4 litres is the molar volume of all gases at STP.*

2.4.6 Problem of Atomic Masses Reconsidered

Having discussed the mole concept, we shall now re-examine the problem of determining relative atomic masses and molecular formulae. The reasoning outlined in section 2.4.3 is limited to determining the atomic masses and molecular formulae of gaseous elements and compounds. The extension of the method to a wider class of substances was made by the Italian chemist Stanislao Cannizzaro (1860) who made an ingenious use of Avogadro's hypothesis in the following manner.

The 'equal volume–equal particle' idea enables direct experimental determination of relative molecular masses from gas density measurements. Since density is mass per unit volume, the densities of two gases measured at the same temperature and pressure are in the same ratio as their molecular masses. We should, therefore, be able to determine the molecular masses of compounds by the measurement of their densities in the vapour phase. If the densities of gases are measured relative to hydrogen gas (at the same temperature and pressure), then the molecular masses will be 2·02 times the respective densities. Since a molecule contains whole numbers of atoms, a mole of molecules of a compound must contain an integral number of moles of atoms of each of its constituent elements. Hence, if one determines the mass of an element (per mole of a compound) in a large number of compounds, then the masses ought to be integral multiples of some number. If the number of compounds studied this way is large, then the largest common factor of masses of the element is most likely the mass of one mole of that element; this immediately yields the atomic mass of the element in amu.† Let us see how Cannizzaro's analysis is applied in practice. Suppose we wish to determine the atomic mass of chlorine. Table 2.2 lists the experimental data on a large number of chlorine compounds. The largest common factor is 35·5 g which, therefore, is the mass of one mole of chlorine atoms (i.e. atomic mass of chlorine atom is 35·5 amu).

The relative atomic mass scale based on the oxygen atomic mass of 16·00 amu was in use until the beginning of the century. However, when in 1910 it was discovered that atoms of an element

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*This statement is only approximately true for real gases as shown in Chapter 6.

†The logic of this method can be further clarified by the following problem. Suppose we have six bags, each containing different (and unknown) number of stones. If the masses of the bags are 750, 1250, 250, 100, 1000 and 300 grams and all the stones are of equal mass, we can obtain the mass of a stone without actually weighing it or without opening the bags. It is obvious that since there are no fractional stones, the total mass in each bag must be an integral multiple of the mass of a single stone. In the present case, the mass is most likely to be 50 g as it is the highest common factor. We say ' most likely ' because answers like 25 g or 10 g cannot be ruled out, but they are unlikely. If 25 g were the mass, it would be surprising that none of the bags have a mass (e.g. 175 g) which is an integral multiple of 25 but not of 50.

Table 2.2 Various Chlorine Compounds used by Cannizzaro to Deduce the Atomic Mass of Chlorine[1]

Compound	Molecular mass[2] (amu)	Molar mass (g)	Mass of chlorine per molar mass (g)
Chlorine	71	71	$71 = 2 \times 35.5$
Hydrogen chloride	36.5	36.5	$35.5 = 1 \times 35.5$
Mercuric chloride	271	271	$71 = 2 \times 35.5$
Ethyl chloride	64.5	64.5	$35.5 = 1 \times 35.5$
Arsenic chloride	181.5	181.5	$106.5 = 3 \times 35.5$
Phosphorous chloride	138.5	138.5	$106.5 = 3 \times 35.5$
Tin chloride	259.6	259.6	$142 = 4 \times 35.5$
Silicon chloride	170	170	$142 = 4 \times 35.5$
Aluminium chloride	267	267	$213 = 6 \times 35.5$
Iron chloride	325	325	$213 = 6 \times 35.5$

[1]Note that the data do not rule out a value of 17.75 for chlorine. If this was the true value, then the number of moles of chlorine in each of the compounds will be doubled (e.g. in hydrogen chloride it will become 2, in mercuric chloride it will be 4 and so on). Then it would be difficult (but not impossible) to understand, why no compounds of chlorine exist which have 1 or 3 moles of chlorine. Thus 17.75 (or any other fraction of it) is an unlikely value.

[2]Obtained from vapour density measurements relative to hydrogen gas.

can have different masses (isotopes of the element),[*] two atomic mass scales came into being which differed in their choice of the standard. The so-called chemical scale took 16.00 amu as the average mass of the natural mixture of oxygen isotopes, while the physical scale was based on 16.00 amu as the mass of the oxygen isotope of atomic number 16. The modern scale, agreed upon by chemists and physicists in 1961, uses the carbon isotope of atomic mass 12 (written as ^{12}C) as the standard with an assigned value of 12.000 amu. The relative atomic mass of any atom in amu is redefined as the ratio of the mass of that atom to 1/12 of the mass of ^{12}C atom. The current values of atomic masses are given on the inside cover of the book.

With the knowledge of atomic masses, the Avogadro number N_0 ($= 6.02 \times 10^{23}$), and the mole concept, it is easy to calculate the masses of single atoms in grams.

Example 2.1 Calculate the mass of a ^{12}C atom and of a silver atom.

Mass of a ^{12}C atom = 12.000 amu
∴ mass of one mole of ^{12}C atoms = 12.000 g
This means that mass of 6.02×10^{23} ^{12}C atoms = 12.000 g

$$\text{The mass of a single } ^{12}C \text{ atom} = \frac{12.000}{6.02 \times 10^{23}} = 1.99 \times 10^{-23} \text{ g}$$

In the same manner, since the atomic mass of silver is 107.87,

$$\text{the mass of a silver atom} = \frac{107.87}{6.02 \times 10^{23}} = 17.93 \times 10^{-23} \text{ g}$$

[NOTE: For silver, the mass represents the weighted average of isotopic masses.]

Example 2.2 Determine the number of atoms in 1.793×10^{-6} g of silver.

Mass of a silver atom = 17.93×10^{-23} g

$$\therefore \text{number of atoms of silver in } 1.793 \times 10^{-6} \text{ g of silver} = \frac{1.793 \times 10^{-6}}{17.93 \times 10^{-23}} = 10^{16}$$

[*]Isotopes are discussed in Chapters 3 and 19.

2.4.7 Determination of Empirical and Molecular Formulae

We are now in a position to dertermine the chemical formulae of substances in a systematic manner. Formulae are of two types.* The first is the *empirical formula*; it tells the relative number of different types of atoms present in a compound. The second type is known as the *molecular formula;* it expresses the exact number of different atoms in a compound. For example, CH is the empirical formula of benzene and C_6H_6 is its molecular formula.

The empirical formula of a compound can be calculated from (*i*) chemical analysis of the compound and (*ii*) atomic masses of the relevant elements. The chemical analysis which is obtained from experimental measurements, is usually expressed as percentage composition (by mass) of the elements in the compound. (Oxygen percentage is usually not given explicitly; it is obtained by subtracting the sum of the percentages of all the other elements from 100.) To calculate the empirical formula, the first step is to convert the given percentage composition to mole composition. This is done by dividing the mass of each element by its atomic mass. From the mole composition we can determine the mole ratio between different elements in the compound. Any fraction in mole ratio is then removed by dividing or multiplying by a suitable number.

Example 2.3 An organometallic compound on analysis was found to contain, $C=64\cdot4\%$, $H=5\cdot5\%$ and $Fe=29\cdot9\%$. Determine its empirical formula.

The sum of percentages is $99\cdot8(\simeq 100)$. Therefore no oxygen is present. Percentage composition by mass is $64\cdot4\% C : 5\cdot5\% H : 29\cdot9\% Fe$.

Mole ratio: $\dfrac{64\cdot4}{12} C : \dfrac{5\cdot5}{1} H : \dfrac{29\cdot9}{55\cdot8} Fe = 5\cdot37 C : 5\cdot5 H : 0\cdot535 Fe$.

Dividing by $0\cdot535$, we get mole ratio $= 10 C : 10 H : 1 Fe$.
Therefore, empirical formula is $C_{10}H_{10}Fe$.

Example 2.4 Four grams of copper chloride on analysis was found to contain $1\cdot890$ g of copper (Cu) and $2\cdot110$ g of chlorine (Cl). What is the empirical formula of copper chloride?

$$\text{Percentage of copper in copper chloride} = \frac{1\cdot890}{4} \times 100 = 47\cdot3\%$$

$$\text{Percentage of chlorine in copper chloride} = \frac{2\cdot110}{4} \times 100 = 52\cdot7\%$$

Percentage composition is $47\cdot3\%$ Cu and $52\cdot7\%$ Cl.

Mole ratio $= \dfrac{47\cdot3}{63\cdot6} Cu : \dfrac{52\cdot7}{35\cdot5} Cl = 0\cdot743 Cu : 1\cdot485 Cl$

Dividing by $0\cdot743$, mole ratio $= 1 Cu : 2 Cl$
Therefore, the empirical formula is $CuCl_2$.

The molecular formula of a compound can be calculated from (*i*) the molecular mass of the compound (which is determined experimentally) and (*ii*) the empirical formula of the compound (calculated as shown above).

Example 2.5 The molecular mass of benzene is 78 and its percentage composition is $92\cdot3\%$ C and $7\cdot69\%$ H. Determine the molecular formula of benzene.

Percentage composition $= 92\cdot3\%$ C $: 7\cdot69\%$ H

Mole ratio $= \dfrac{92\cdot3}{12} C : \dfrac{7\cdot69}{1} H = 7\cdot69 C : 7\cdot69 H$

*A third type called the structural formula will be discussed later in section 2.7.3

Dividing by 7·69 gives 1C : 1H. Therefore, the empirical formula is CH or the molecular formula is $(CH)_n$.

Empirical formula mass $=12+1=13$ amu
$n=$ mol. mass/13 $\qquad =78/13=6$

Therefore, the molecular formula is C_6H_6.

The calculations can be reversed to obtain the molecular mass if the molecular formula of a compound is known. Also, knowing the molecular formula, one can determine the number of moles (or number of molecules) in a given amount of that compound.

Example 2.6 Compute the mass of one molecule and the molecular mass of C_6H_6 (benzene).

$$
\begin{aligned}
\text{Mass of one molecule of } C_6H_6 &= 6 \times \text{mass of C atom} + 6 \times \text{mass of H atom} \\
&= 6 \times 1 \cdot 99 \times 10^{-23} + 6 \times 1 \cdot 66 \times 10^{-24} \\
&= 11 \cdot 94 \times 10^{-23} + 9 \cdot 96 \times 10^{-24} \\
&= 12 \cdot 94 \times 10^{-23} \text{g} \\
\text{Molecular mass} &= 6 \times \text{atomic mass of C} + 6 \times \text{atomic mass of H} \\
&= 6 \times 12 \cdot 00 + 6 \times 1 \cdot 008 \\
&= 72 + 6 \cdot 048 = 78 \cdot 048 \text{ amu}
\end{aligned}
$$

Example 2.7 Calculate the number of moles and the number of molecules in 8·516 g of ammonia (NH_3)

$$
\begin{aligned}
\text{Molecular mass of } NH_3 &= 14 \cdot 007 + 3 \times 1 \cdot 008 \\
&= 17 \cdot 031 \text{ amu} = 17 \cdot 031 \text{ g/mol ammonia} \\
\text{Therefore 8·516 g of ammonia} &= 8 \cdot 516 \text{ g}/17 \cdot 031 \text{ g/mol ammonia} \\
&= 0 \cdot 5 \text{ mol ammonia}
\end{aligned}
$$

1 mol of a substance has $6 \cdot 02 \times 10^{23}$ molecules.
Therefore, 0·5 mol has $3 \cdot 01 \times 10^{23}$ molecules.

Example 2.8 Calculate the number of grams of oxygen in 0·10 mol of $Na_2 CO_3 \cdot 10H_2O$.

One mol of $Na_2CO_3 \cdot 10H_2O$ has 13 mol of oxygen atoms. Therefore, in 0·1 mol of $Na_2 CO_3 \cdot 10H_2O$, there will be 1·3 mol of oxygen atoms.

One mol of oxygen atoms $\quad = 16$ g
Therefore, 1·3 mol of oxygen atoms $= 16 \times 1 \cdot 3 = 20 \cdot 8$ g

2.5 THE CHEMICAL EQUATION AND STOICHIOMETRY

If the substances taking part in a chemical reaction are represented by their molecular formulae, the chemical reaction can be expressed in the form of a chemical equation. Equations provide a powerful symbolic notation to express qualitative and quantitative details of chemical transformations. The quantitative aspect, dealing with the mass and volume relations among reactants and products, is termed *stoichiometry*.* We shall now discuss how a chemical equation is written and what information it conveys before proceeding to stoichiometric calculations.

2.5.1 Writing a Balanced Chemical Equation

The chemical reaction between hydrogen and oxygen to produce water can be written as, hydrogen + oxygen = water. However, this cumbersome way of expressing a chemical event can be improved by using appropriate formulae

*Stoichiometry is derived from Greek words meaning ' to measure an element '.

for the species involved. Thus, the above reaction can be alternately written as, $H_2 + O_2 = H_2O$. This equation is not consistent with the law of conservation of mass because there are two atoms of oxygen on the left-hand side while there is only one atom of oxygen on the right-hand side. This means that for a chemical equation to be valid, the number of atoms of each element must be same on both sides of the equation. An equation satisfying this requirement is called a balanced chemical equation;* balancing can be done by supplying suitable coefficients to any of the species on either side of an equation. Thus, the balanced equation for the above mentioned reaction can be written in any of the following forms:

$$H_2 + \tfrac{1}{2}O_2 = H_2O \tag{i}$$
$$2H_2 + O_2 = 2H_2O \tag{ii}$$
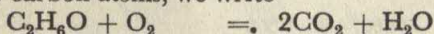$$4H_2 + 2O_2 = 4H_2O \tag{iii}$$
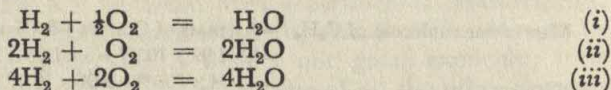
However, by convention, equations are written in a form in which the coefficients are the smallest whole numbers. The reaction between hydrogen and oxygen to give water is thus represented by equation (*ii*).
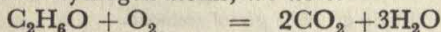
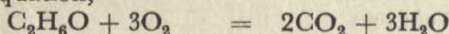As another example of balancing an equation, we consider the reaction,

$$C_2H_6O + O_2 \qquad = \qquad CO_2 + H_2$$

ethyl alcohol + oxygen = carbon dioxide + water

To balance carbon atoms, we write

$$C_2H_6O + O_2 =. 2CO_2 + H_2O$$

and to balance hydrogen atoms, we write

$$C_2H_6O + O_2 = 2CO_2 + 3H_2O$$

Oxygen atoms can be balanced by multiplying O_2 by 3. Thus, we have the balanced equation,

$$C_2H_6O + 3O_2 = 2CO_2 + 3H_2O$$

It is frequently convenient to know the physical state (i.e. solid, liquid or gas) of each reactant and product. This information will be a necessity, when we later discuss the energy changes during chemical reactions. The following abbreviations are used to indicate the physical state of the participants: $(s) =$ solid, (l) = liquid, (g) = gas or vapour, (aq) = aqueous solution.

Thus, the reactions given earlier can be written more precisely as,

$$2H_2(g) + O_2(g) = 2H_2O(g)$$

and $C_2H_6O(l) + 3O_2(g) = 2CO_2(g) + 3H_2O\ (l)$
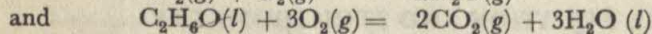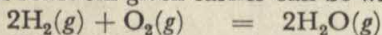
Additional information about heat absorbed or evolved, temperature, pressure etc., can also be incorporated in a chemical equation. This will be considered later at appropriate places.

2.5.2 Significance of Chemical Equations

A balanced equation contains much quantitative information because it can be interpreted in a number of ways. Let us first consider reactions in which all the participants are gases. For instance, the equation, $2H_2(g) + O_2(g) = 2H_2O(g)$, means:

    2 molecules of hydrogen + 1 molecule of oxygen = 2 molecules of steam,

or, $2(6 \cdot 02 \times 10^{23})$ molecules of hydrogen + $1(6 \cdot 02 \times 10^{23})$ molecules of oxygen = $2(6 \cdot 02 \times 10^{23})$ molecules of steam

or, 2 mol of hydrogen + 1 mol of oxygen = 2 mol of steam

---

*When equations involving charged species (e.g. ions) are written, they must satisfy the charge conservation also. This aspect will be considered in Chapter 12.

or, 4 g of hydrogen + 32 g of oxygen = 2 g of steam

or, 44·8 litres of hydrogen + 22·4 litres of oxygen = 44·8 litres of steam

Thus, a chemical equation for a gaseous reaction gives quantitative details about reactants and products in terms of (i) molecules (or atoms), (ii) moles, (iii) grams, and (iv) volumes (if any of the participants are in the gaseous form).

Example 2.9 Hydrogen chloride on oxidation with oxygen gives water and chlorine. How many litres of chlorine at STP can be obtained starting with 36·45 g of HCl?

In order to solve such problems, the first important step is to write a balanced equation. To do this we write a skeleton equation on the basis of experimental observation. For the above reaction the skeleton equation is:

$$HCl + O_2 = Cl_2 + H_2O$$

On balancing, we get,

$$4HCl + O_2 = 2Cl_2 + 2H_2O$$
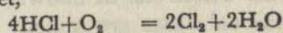
i.e. 4 mol of HCl = 2 mol of chlorine

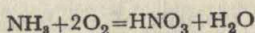36·45 g of HCl = 1 mol of HCl

∴ 1 mol of HCl = 0·5 mol of chlorine

But 1 mol of chlorine at STP = 22·4 litres

∴ 0·5 mol at STP = 11·2 litres

Example 2.10 Ammonia is catalytically oxidised by oxygen to give nitric acid and water. How much ammonia and oxygen are required to manufacture 63 quintals of nitric acid daily? What will be their volumes at STP ?

$$NH_3 + 2O_2 = HNO_3 + H_2O$$

One mol of nitric acid is produced from one mol of ammonia and 2 mol of O_2

63 quintals of nitric acid = 63×10^5 g

63 g of nitric acid = 1 mol of nitric acid

Therefore, 63×10^5 g of nitric acid = 10^5 mol of nitric acid; 10^5 mol of nitric acid will require 10^5 mol of ammonia and 2×10^5 mol of O_2.

1 mol of ammonia = 17 g

Therefore, 10^5 mol of NH_3 = 17×10^5 g = 17 quintals

1 mol of $O_2 = 32$ g

Therefore, 2×10^5 mol of O_2 = 64×10^5 g = 64 quintals

Volume of ammonia required (at STP) = $22·4 \times 10^5$ litres

Volume of oxygen required (at STP) = $44·8 \times 10^5$ litres

Concentration units: Most reactions are carried out by dissolving reactants in a suitable solvent. As mole is the basic chemical unit, the concentration of the dissolved substance is usually specified in terms of number of moles of solute. (In a solution, the substance present in a smaller amount is known as solute while the substance present in larger amounts is known as solvent.) One concentration unit, quite common in analytical chemistry, is called *molarity* (M). It is defined as the number of moles of solute per litre of solution.

Example 2.11 Calculate the molarity of the following solutions: (a) 30·0 g of NaOH present in 1·00 litre of NaOH solution and (b) 5·475 g of HCl present in 750 ml of HCl solution.

In (a), there are 30·0/40·0 = 0·75 mol of NaOH present in 1 litre of the solution. Therefore, the molarity of the solution is 0·75M.

In (b), 5·475 g of HCl are present in 750 ml, or 7·3 g of HCl are present in 1 litre.
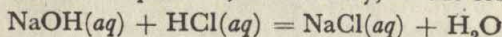
∴ Molarity of the solution = $\dfrac{7·3}{36·5} = 0·2M$

To illustrate the significance of chemical equation for reactions in solution, we consider the reaction between sodium hydroxide and hydrochloric acid solution in water. The equation* is

$$NaOH + HCl = NaCl + H_2O$$
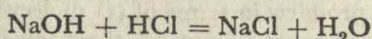
The nature of the solvent is specified, if necessary, in the following manner.

$$NaOH(aq) + HCl(aq) = NaCl(aq) + H_2O$$

If solvent is not stated, it is understood that water is the medium since the majority of solution reactions take place in aqueous medium.

The above equation can be interpreted in terms of number of molecules, or number of moles, or amount in grams, of the reactants and the products in exactly the same way as shown earlier. However, unlike equations for the gaseous reactions, the above equation gives no information about the volumes of the reacting solutions. These can be known, if the molarities of the solutions are given. If equimolar solutions are mixed, then the volumes must also be equal; if the solutions are not equimolar, the volumes can be easily calculated.

Example 2.12 How many litres of $0.2M$ solution of HCl would completely react with 0.1 litre of $0.75M$ NaOH solution.

Since equal volumes are needed for equimolar solutions, it follows that

$$\frac{0.75}{0.2} \times 0.1 = 0.375 \text{ litre of HCl solution would be required for completion of reaction.}$$

It should be realised that molarity of a solution depends on temperature because it is defined as the number of moles of solute per *unit volume* of solution and volume of a solution depends upon temperature. Therefore, for accurate work, temperature must be specified when molarity is used as the concentration unit. If one wishes to use temperature-independent units, then concentration is expressed either as *mole fraction* or as *molality*. These units are particularly useful for discussing the influence of solute on the properties of a solvent or for discussing the overall properties of a solution.

If a solution consists of two constituents A and B such that N_A and N_B are the number of moles of A and B respectively, then their *mole fractions* X_A and X_B are defined as

$$X_A = \frac{N_A}{N_A + N_B} \qquad X_B = \frac{N_B}{N_A + N_B}$$

It is not necessary to specify which of the constituents is a solvent. If several constituents are present the definition can be easily generalised. It follows from the definition, that the sum of mole fractions of all the components of a solution is unity. For example, for the two-component case considered

$$X_A + X_B = \frac{N_A}{N_A + N_B} + \frac{N_B}{N_A + N_B} = 1$$

Example 2.13 Calculate the mole fraction of water in a NaOH solution consisting of 80 g of NaOH and 54 g of water.

*We shall study later that sodium hydroxide as well as hydrochloric acid are present as ions in aqueous solutions. The reaction between such species is therefore represented by ionic equations. See Chapter 11 for further details.

$$\text{No. of moles of NaOH} = \frac{80}{40} = 2 \text{ mol}$$

$$\text{No. of moles of H}_2\text{O} = \frac{54}{18} = 3 \text{ mol}$$

$$\therefore X_{\text{H}_2\text{O}} = \frac{3}{5} = 0.6$$

The *molality* (*m*) of a solution is defined as the number of moles of solute per kilogram of solvent. Since the definition involves mass of solvent, molality is obviously independent of temperature.

Example 2.14 Calculate the molality of NaCl solution prepared by dissolving 29·25 g of NaCl in 100 g of water.

$$\text{No. of moles of NaCl in 100 g of water} = \frac{29·25}{58·5} = 0·5 \text{ mol}$$

$$\text{No. of moles of NaCl in 100 g of water} = \frac{0·5 \times 1000}{100} = 5 \text{ mol}$$

Therefore the concentration of NaCl solution is 5*m*.

If the density of a solution is known molality can be converted into molarity or vice versa.

Example 2.15 The molarity of a solution of sodium carbonate is 0·408 mol/litre at 20°C. Calculate the molality of the solution. (Density of solution at 20°C = 1·0816 g/ml)

From the density it follows that mass of 1 litre of Na_2CO_3 solution = 1081·6 g

mass of Na_2CO_3 in 1 litre solution   = 0·408 mol
        = 43·26 g

$\therefore$ mass of water in 1 litre solution   = 1081·6 − 43·26
        = 1038·4 g

Now, 1038·4 g of water contains = 0·408 mol of Na_2CO_3

$\therefore$ 1000 g of water contains $\dfrac{0·408}{1038·4} \times 1000 = 0·393$ mol

Hence molality of Na_2CO_3 solution = 0·393 *m*

It may be pointed that the concept of molarity, in a strict sense, applies to only such substances which exist in the form of molecules (molecular solutes). However, it is quite common to extend the use of molarity to include even those solutions which contain non-molecular solutes (e.g. electrolytes which exist in solution as ions). If one wishes to be very precise, the term *formality* is employed instead of molarity. The calculation procedure is similar in this case with formula mass playing the role of molecular mass.

Another concentration unit which finds great many applications for reactions in solutions containing ions is *normality*(*N*). Normality is related to molarity by a small integer (usually from 1 to 5), but the tricky thing about this concentration unit is that normality of a compound depends upon the reaction in which the compound is participating. This unit is used in connection with acid–base and oxidation–reduction reactions discussed in Chapters 11 and 12.

2.6 PERIODIC TABLE

The finalisation of a consistent scale of atomic masses around 1860 initiated rapid advance of chemistry on several fronts, the most important one being the construction of the periodic table of elements. The periodic table grew out of the investigations of several chemists to find a correlation between atomic masses of elements and their physical and chemical properties. There was no logical justification to expect such a correlation in the mid-19th century, but this is one of the many examples in science where a great idea is born out of intuition rather than reason and logic.

2.6.1 The Periodic Law

Attempts to find a link between atomic masses and chemical behaviour culminated in *Mendeleev's discovery* in 1869 that *properties of elements as well as the formulae and properties of their compounds are periodic functions of atomic masses.* This statement is known as the *periodic law*. At the time when this law was proposed, only about sixty elements were known, which, when successively arranged in the order of increasing atomic mass, certainly did not exhibit any periodicity. Mendeleev argued with remarkable insight that not all the elements had been discovered and left blanks for the undiscovered elements. He then proceeded to arrange the known elements in a tabular form such that elements occurring in the same column of the table, called the *periodic table*, had similar behaviour. Moreover, he observed that properties like melting and boiling points, chemical reactivity and atomic volume changed systematically and gradually across a row and down a column of the periodic table. He also observed that molecular formulae of the compounds of the elements in various columns were similar. This enabled Mendeleev to predict the properties of many as yet undiscovered elements in the blank spaces of the periodic table on the basis of the properties of the neighbouring elements. Subsequently, when some of these elements were isolated, the close agreement between their actual properties and the predicted ones (see Table 2.3), constituted a triumphant vindication of the correctness of Mendeleev's ideas.

The logical basis of the periodic table became clear in the 1920's when the theory of electronic structure of the atom was developed. This also brought about a revision of the periodic law. The modern version asserts that it is the *atomic number*, and not the *atomic mass*, which is at the root of the periodic behaviour of elements. The most popular form of the periodic table in use today—the so-called long form—is shown in Table 3.5 and the theory of periodic table is discussed in Chapter 3.

The major contribution of the periodic table is that it systematises the study of chemistry. By suitable groupings, it reduces the description of over 100 elements to a description of a few families of elements. Some prominent *families of elements* are the halogens, the noble gases, the alkali metals, the alkaline-earth metals, the transition elements, the rare earths and the actinides. The uses of periodic table will become obvious when we discuss the chemistry of elements in Chapters 16, 17 and 19.

That the periodic table is an indispensable guide to speculation and research is nicely illustrated by the following examples: In the 1920's, need was felt for synthesising an inexpensive compound which would also be odourless, non-toxic, non-inflammable and non-corrosive to take the

place of the various *refrigerants* then in use (all of which had at least one undesirable property). The purely hit and trial approah to such a problem is, of course, hopeless. An American engineer, Thomas Midgley, in 1929 began searching the periodic table for some clues. He noticed that the elements at the right of the table were the only ones which formed compounds volatile enough to act as refrigerants. He also noticed that amongst these compounds, inflammability decreased from left to right while the toxicity decreased from bottom to top. This analysis suggested that compounds of fluorine may be the answer to the problem even though the element itself is highly corrosive and toxic. Midgley decided to test his reasoning by actually synthesising fluorine compounds. Two years later he came up with the first of a large group of ideal refrigerants called *Freon*—which revolutionised commercial refrigeration.

An important use of the periodic classification of elements has been in the preparation of materials with desired properties. Germanium and silicon (group IVA elements) are important materials for electronics industry. Both these elements have a valency (see section 2.7.1) of four just like the first element of this group, carbon. Scientists thought that it would be interesting to simulate the valency of four by a combination of elements of different valencies. For example, a 1:1 compound of two elements with valencies of 3 and 5, 2 and 6 or 1 and 7, would give an average valency of four. It was indeed found that such combinations gave exciting compounds

Table 2.3   Mendeleev's Predictions for the Element Ekasilicon (Germanium)[1]

Property	Tin and its compounds	Silicon and its compounds	Mendeleev's predictions for Ekasilicon	Winkler's report for Germanium
Atomic mass	118·7	28·1	72	72·6
Appearance	White metal or gray non-metal	Gray, diamond-like	Gray metal	Gray metal
Melting point	232°C	1410°C	High	958°C
Density	7·31	2·42	5·5	5·36
Action of acid and alkali	Slow attack by conc. HCl, attacked by HNO_3; inert to lye	Acid resistant; slow attacked by alkali	Acid and alkali resistant	Not attacked by HCl or lye; attacked by HNO_3
Oxide formula and density	SnO_2, 7.0	SiO_2, 2·65	EsO_2, 4·7	GeO_2, 4·70
Sulphide formula and properties.	SnS_2, insoluble in water, soluble in ammonium sulphide solution	SiS_2, decomposes in water	EsS_2, insoluble in water, soluble in ammonium sulphide	GeS_2, insoluble in water, soluble in ammonium sulphide
Chloride formula	$SnCl_4$	$SiCl_4$	$EsCl_4$	$GeCl_4$
Boiling point	114°C	57·6°C	100°C	83°C
Density	2·23	1·50	1·9	1·88
Preparation of element	Reduction of SnO_2 with carbon	Reduction of K_2SiF_6 with sodium	Reduction of EsO_2 or K_2EsF_2 with sodium.	Reduction of K_2GeF_6 with sodium

[1] The agreement between Mendeleev's predicted properties of germanium (which he called ekasilicon) and the actual properties of the same element as reported by Winkler are spectacular. The predictions of Mendeleev were not wild speculations but were based on systematic interpolation of the available data on silicon and tin, the upper and lower neighbours of the unknown element. The success ' proved ' for once and for all that there exists a relation between atomic mass and properties though modern theory shows that this connection is fortuitous. The real link is between atomic number and properties. For details see Chapter 3.

of technological importance. Thus, groups III–V compounds (AlP, GaAs, InSb) and group II–VI compounds (ZnS, CdSe, HgTe) came into being through a judicious use of the periodic table.

2.7 EVOLUTION OF STRUCTURAL CHEMISTRY

The mid-19th century also saw the introduction and evolution of the concept of structure which forms the backbone of modern chemical thinking.* This idea developed in the following manner.

2.7.1 Concept of Valence

As already shown, the atomic mass scale permitted the deduction of molecular formulae of substances. When thousands of compounds were analysed this way, certain regularities became apparent in their formulae. Thus, the formulae, H_2, HCl, LiH, etc., suggest that an atom of hydrogen generally combines with no more than a single atom of any other element. Such observations led to the notion of *valence* which was defined as the combining capacity of an atom. Hydrogen atom was assigned the valence of one (univalent). Valences of other atoms could be derived from the formulae of the binary compounds of the elements. For example, the formula HCl means that chlorine is also univalent, while H_2O, NH_3, and CH_4 show that oxygen, nitrogen, and carbon atoms are di-, tri-, and quadri-valent respectively. Important support for the idea of valence came from the internal consistency in its usage. For example, if chlorine is univalent, then $MgCl_2$ makes magnesium atom divalent. Further, since hydrogen is univalent, the binary compound of magnesium and hydrogen (magnesium hydride) must have the formula MgH_2, as is indeed observed. The valences of some common elements are given in Table 2.4.

Table 2.4   Valences of some Elements[1]

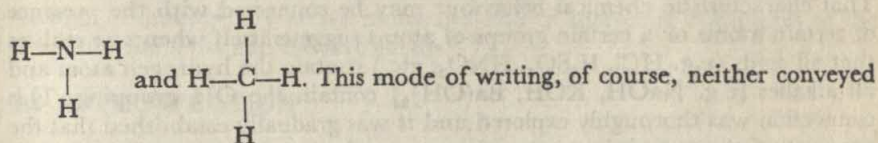| Element	Typical compound	Valence	Element	Typical compound	Valence
H	H_2, H_2O, HCl	1	S	H_2S, CS_2	2
F	F_2, HF, ClF	1	N	NH_3, NF_3	3
Cl	Cl_2, CCl_4, Cl_2O	1	B	BCl_3, BF_3	3
Br	Br_2, HBr, PBr_3	1	P	PH_3, PCl_5	3
I	I_2, HI, ICl	1	C	CH_4, CO_2, CCl_4	4
O	H_2O, Cl_2O, CO_2	2	Si	$SiCl_4$, SiO_2	4

[1]Though not stated in the text, many elements show more than one valence. For instance, phosphorus also has valence of five as in PCl_5. Variable valence was entirely incomprehensible on the basis of classical atomic theory.

2.7.2 Chemical Bond

The concept of valence became useful enough that chemists started representing it pictorially. An atom was imagined as having as many arms or hooks as its valence number and molecule formation was visualised as taking place through the interlinking of these arms or hooks. Thus, hydrogen, oxygen, nitrogen, and carbon atoms were imagined as having one, two, three and four

*It has been remarked that nowadays all the chemists spend part of their time, and part of the chemists spend all their time, thinking about structure.

hooks respectively. This interlinking of hooks, called a *chemical bond*, was depicted on paper by writing the formulae H_2, H_2O, NH_3, and CH_4 as H—H, H—O—H,

$$\overset{\displaystyle H}{\underset{\displaystyle H}{H—N—H}} \quad \text{and} \quad \overset{\displaystyle H}{\underset{\displaystyle H}{H—C—H}}.$$ This mode of writing, of course, neither conveyed

nor implied any information about the nature and direction of the valence bonds or to the mechanism of molecule formation. The deeper understanding of chemical bond had to await development of the electronic theory of atoms and molecules (see Chapters 3 and 4). Double and triple bonds (multiple bonds) were introduced to preserve the characteristic valences in certain molecules. For instance, carbon dioxide (CO_2) and acetylene (C_2H_2) were written as $O=C=O$ and $H—C\equiv C—H$ so as to retain univalency of hydrogen, bivalency of oxygen, and quadrivalency of carbon. Thus, the ordering of atoms in a molecule acquired significance since any other ordering in CO_2 and C_2H_2 would violate the assigned valences.

2.7.3 Isomerism and the Idea of Structural Formulae

The suggestion that atoms are ordered in a molecule received conclusive support with the discovery of isomerism, a widely occurring phenomenon in carbon compounds. *Isomerism** means the existence of two or more compounds, called *isomers*, having the same molecular formula but different properties. This experimental fact can be understood by assuming that physico-chemical properties of a compound are not only controlled by the number and type of atoms but also by the ordering of atoms in the molecule. The sequence of atoms in a molecule is indicated by the structural formula of the molecule. As an example, consider the two compounds butane and isobutane which have different properties but the same molecular formula, C_4H_{10}. Consistent with the quadrivalency of carbon and the monovalency of hydrogen, it is possible to write two different structural formulae namely
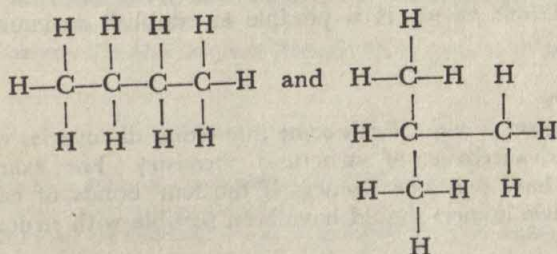
But how do we decide which structural formula is to be assigned to butane and which to isobutane? To answer this question, we shall have to examine the relation between structure and behaviour.

*Isomerism in organic molecules is discussed in Chapter 5 and in inorganic molecules in Chapter 17.

2.7.4 Chemical Structure and Chemical Reactivity: The Idea of Functional Groups

That characteristic chemical behaviour may be connected with the presence of certain atoms or a certain groups of atoms suggests itself when one realises that all acids (e.g. HCl, H_2SO_4, HNO_3, etc.) contain the hydrogen atom and all alkalies [e.g. $NaOH$, KOH, $Ba(OH)_2$] contain the OH grouping. This connection was thoroughly explored and it was gradually established that the presence of characteristic groups of atoms, and even characteristic structural features (e.g. single bond, double bond), conferred characteristic reactivities on the molecule. This is the origin of the idea of *functional groups*. For instance, it is found that all compounds containing double bond react with ozone while

$$\overset{\text{O}}{\overset{\|}{\text{—C—H}}}$$

all compounds containing —C—H group (called aldehydic group) react with potassium permanganate to give acids. Thus, the double bond and the aldehyde group are examples of functional groups. Some other common examples are listed in Table 2.5 while a more detailed discussion is given in Chpter 5. The idea of functional groups has proved very useful in organic chemistry,
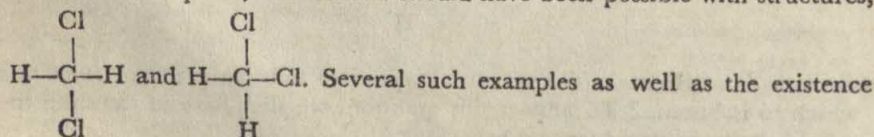
Table 2.5 Some Representative Functional Groups[1]

Functional Group	Name	Functional Group	Name
C=C	double bond	$\overset{\text{O}}{\overset{\|}{\text{—C—C—C—}}}$	ketone
$\overset{\text{O}}{\overset{\|}{\text{—C—H}}}$	aldehyde	$\overset{\text{O}}{\overset{\|}{\text{—C—OH}}}$	carboxylic acid
—C—OH	alcohol		

[1]For fuller discussion, see Chapter 5.

since with a good catalogue of functional group behaviour (derived from analysis of relatively simple cases), it is possible to establish structures of complicated molecules.

2.7.5 Stereochemistry

Further study of isomerism brought forth some interesting discoveries which contributed to the advancement of structural chemistry. For example, CH_2Cl_2 was found to have only one isomer. If the four bonds of carbon were all in one plane, two isomers should have been possible with structures,

$$\overset{\text{Cl}}{\underset{\text{Cl}}{\text{H—C—H}}} \quad \text{and} \quad \overset{\text{Cl}}{\underset{\text{H}}{\text{H—C—Cl}}}.$$ Several such examples as well as the existence

of *optical activity* in carbon compounds (see Chapter 5 for a discussion) forced the conclusion that the four valences of carbon atom are not planar but tetrahedral. This marked the beginning of stereochemistry which is concerned

with the arrangement in space of the atoms in a molecule of given structure. Stereochemical considerations are extremely important to understand the behaviour of biologically active molecules and of inorganic complexes of the transition elements and the rare earths.

2.8 RETROSPECTION

We have covered in this chapter some of the major milestones in the development of the classical atomic-molecular theory. It is indeed remarkable that such a collection of subtle ideas sprang from the data accumulated from experiments performed with simple and unsophisticated apparatus like a flask, beaker, balance, pipette, burette, thermometer, manometer, etc. The classical theory is thus a tribute to the ingenuity, imagination and intuition of its founders like Lavoisier, Dalton, Avogadro, Berzelius, Kekule, vant Hoff, Emil Fischer, Werner and many others. The concepts of atom, molecule, valence and chemical bond, structure, and periodicity, helped chemistry to emerge as a quantitative science and they also contributed directly or indirectly to the rise of chemical technology. However, for all its impressiveness, the classical theory suffered from the major handicap that its concepts were logically uncorrelated. For example, it gave no satisfactory answers to such obvious questions as 'why atoms combine to form molecules?' or 'why atoms exhibit characteristic valence or why in some cases the valence is variable?' or 'why chemical behaviour is periodically related to atomic mass?' and so on. Further, the experimental techniques in use then could only yield qualitative information like the type of ordering of atoms in a molecule, but they were incapable of furnishing quantitative details like sizes and absolute masses of atoms, the distances and angles in molecules, etc. We, therefore, now turn to a discussion of the modern theory which has reduced, if not entirely removed, the limitations of the classical theory.

SUGGESTED READING

B. J. BACKENRIDGE and R. M. ROSENBERG, *The Principles of Physics and Chemistry*, McGraw-Hill Book Co., New York, 1970.

W. F. KIEFFER, *The Mole Concept in Chemistry*, Chapman & Hall Ltd., London 1965.

PROBLEMS

2.1 Find the mass of a single atom of S, Xe, and U in g. How many atoms of each will be required to give a mass of 0.1 g?

2.2 Calculate the molecular masses of the following: XeF_4, H_2SO_4, $K_4Fe(CN)_6$.

2.3 Express in moles: (*a*) 0.17 g of H_2O_2 (hydrogen peroxide); (*b*) 1120 ml of oxygen at STP; and (*c*) 3.12 g of $Al(OH)_3$.

2.4 What will be the mass of each element in 0.1 mol of CaC_2; $CuSO_4 \cdot 5H_2O$, PCl_5, and Fe_2Cl_6.

2.5 Find the empirical formula for the compounds for which following analytical data are available per 100 g of the sample:
   (*i*) $Al = 23.1\%$, $C = 15.4\%$ and $O = 61.5\%$
   (*ii*) $Ca = 25.3\%$, $P = 39.2\%$ and $O = 35.5\%$
   (*iii*) $H = 5.88\%$ and $O = 94.12\%$

2.6 Calculate the mass of each element in 3·92 g of $FeSO_4$, $(NH_4)_2 SO_4$, $6H_2O$. What will be the volume of O_2 at STP in the above sample?

2.7 0·789 g of platinum chloride contains 0·210 g of chlorine and 0·579 g of platinum. Determine the empirical formula of platinum chloride.

2.8 Chlorine can be prepared from the oxidation of HCl by $KMnO_4$ according to the following equation:
$$16HCl + 2KMnO_4 = 2MnCl_2 + 2KCl + 8H_2O + 5Cl_2$$
How many grams of HCl and $KMnO_4$ are required to produce 224 ml. of Cl_2 gas at STP?

2.9 Benzene (C_6H_6) burns in oxygen according to the following equation:
$$2C_6H_6 + 15O_2 = 12CO_2 + 6H_2O$$
How many litres of CO_2 will be produced at STP from 3.9 g of benzene?

2.10 In fertiliser industry, hydrogen is prepared from hydrocarbon by a catalytic reaction represented by the equation:
$$C_nH_{2n+2} + 2nH_2O \xrightarrow{catalyst} nCO_2 + (3n+1)H_2$$
For $n=4$, $29·12 \times 10^4$ litres (STP) of hydrogen are produced daily. What is the daily consumption of the hydrocarbon and steam (H_2O)?

2.11 Acetylene (C_2H_2) is produced from calcium carbide according to the following reaction:
$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$
How many grams of CaC_2 are required to produce 1·12 litre of acetylene?

2.12 Balance the following equations:
(i) $FeS_2 + O_2 = Fe_2O_3 + SO_2$
(ii) $HNO_2 = NO + NO_2 + H_2O$
(iii) $Co_3O_4(s) + H_2 = Co + H_2O$
(iv) $C_6H_8 + O_2 = CO_2 + H_2O$
(v) $H_2 + CO = C_2H_6O + H_2O$
(vi) $NH_3 + O_2 = H_2O + NO$

2.13 The oxidation of glucose is represented by the equation:
$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$$
What is the volume of oxygen consumed and carbon dioxide produced per gram of glucose oxidised, at 1 atm pressure and 298 K?

2.14 Suggest the structural formulae for the compounds (a) water, H_2O; (b) hydrazine, N_2H_4; (c) ammonia, NH_3; and (d) hypochlorous acid, HOCl, using the valencies given in the text.

2.15 In terms of the tetrahedral carbon atom, describe the structures of ethylene, $CH_2=CH_2$, and n-propane, $CH_3—CH_2—CH_3$.

3
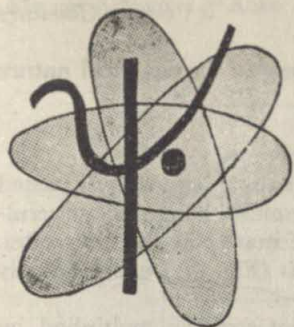
Electronic
Structure of Atoms

I was led to investigation on this subject by having come to the conclusion that when a gas conducts electricity some of its molecules have been split up. . . . It was not until 1897 . . . that I found that one of the bodies into which the molecules split up, the one carrying the negative charge, is something totally different from an atom and is indeed smaller in mass than one thousandth part of the smallest atom known.

J J Thomson

We shall now discuss the electronic structure of atoms and the relation of electronic structure to atomic properties. We begin by recounting some of the brilliant experiments, performed around the turn of the 20th century, which established that an atom is not the indestructible, structureless entity as Dalton had envisaged, but that it is composed of negatively charged electrons and positively charged nucleus. The primary concern at this time was to explain (*i*) the stability of the atom in terms of its sub-atomic constituents and (*ii*) the origin and the nature of the characteristic electromagnetic radiation emitted by different atoms. The first tentative step in this direction was taken by Niels Bohr in 1913, but a completely satisfactory understanding of atomic structure eluded scientists until the theory of quantum mechanics was formulated in 1925–26. After tracing the events which led to the new theory, we shall present the main features of the quantum description. We shall then apply these ideas to describe the electronic structure of atoms and show how it leads to a deeper understanding of the periodic table. We shall conclude this chapter by correlating atomic behaviour with atomic structure—a major triumph of the modern approach.

3.1 EVIDENCE FOR THE ELECTRICAL NATURE OF THE ATOM

The earliest evidence for the electrical nature of matter came from experiments on frictional electricity when it was found that substances like glass or ebonite when rubbed with silk or fur generated electricity. Although these observations paved the way for a detailed understanding of electromagnetic phenomena,

they did not directly contribute to the understanding of the electrical nature of atoms and molecules.

3.1.1 Faraday's Experiments on Electrolysis

It was first noticed by Michael Faraday in the 1830's that if electricity is passed through a solution of an electrolytic conductor, chemical changes occur resulting in the liberation, dissolution, or deposition of matter at the electrodes. Faraday investigated this phenomenon of *electrolysis* (**Fig.** 3.1) quantitatively and the results can be stated in the following form:

(*i*) If a fixed quantity of electricity (i.e. current strength multiplied by passage time) is circulated through a cell, it produces (or destroys) a fixed amount of a particular substance at an electrode. Current is defined as flow of charge per unit time and the product of current (in amperes) with time (in seconds), therefore, measures the amount of charge (in *coulombs*).* The term 'quantity of electricity' thus really means the amount of charge; we can alternatively state that a fixed number of coulombs liberate a fixed amount of matter at an electrode.

(*ii*) The numbers of moles of various substances evolved, dissolved or deposited at an electrode by a fixed quantity of electricity are in the ratio of small integers.
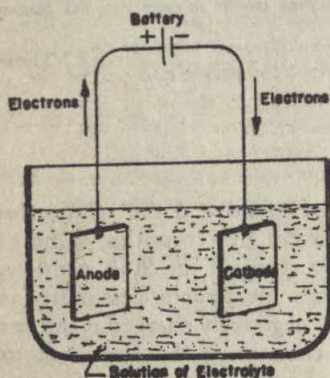

Fig. 3.1 An electrolysis cell

These statements, known as the *Faraday's laws* of *electrolysis*, may be illustrated by an example. It is observed that if 96,487 coulombs† are circulated through a cell containing fused sodium chloride, 1 mol of sodium is deposited at the cathode and ½ mol of chlorine (Cl_2) gas is evolved at the anode. These amounts remain fixed as long as the quantity of electricity is 96,487 coulombs.

The laws of electrolysis are ·strikingly reminiscent of the laws of definite and multiple proportions, but this similarity was not exploited for nearly fifty years until Stoney in 1874 stated that Faraday's laws for the interaction between electricity and matter are counterparts of the laws of chemical combination between matter and matter. He then argued that since the latter laws suggest the atomic nature of matter, the former should imply the atomic nature of electricity. Stoney named the 'atoms' of electricity as *electrons*.

3.1.2 Study of Gaseous Discharge

The passage of current through a gas provided further information about the nature of electrons. Under ordinary conditions, gases are poor conductors. However, if a gas is taken in a sealed tube to which two electrodes are attached (see Fig. 3.2) and if the gas pressure in the tube is reduced to about 10^{-2} atm, the gas becomes conducting on applying high voltage (5000–10,000 volts)

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*The cgs unit of charge, much used in atomic structure, is statcoulomb or esu (electrostatic unit). The conversion factor between the two units is given by 1 coulomb $= 3 \times 10^9$ esu.

†This can be obtained by passing a current of 10 amperes for 9648·7 seconds or 5 amperes for $2 \times 9648·7$ seconds or any other appropriate combination.
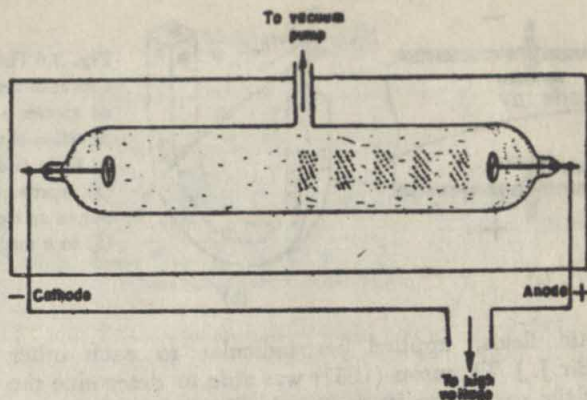
Fig. 3.2 A gas discharge tube. The region near the anode glows at very low pressure while a dark region, known as Crookes' dark space, fills the remaining space. Cathode rays move from left to right. The colour of the glowing region depends upon the nature of the residual gas.

to the electrodes. The gas is found to emit light under these conditions, the colour of the light depending upon the nature of the gas.* The emission of light ceases as the pressure is reduced to about 10^{-4} atm, but the gas continues to conduct electricity and the glass wall of the tube glows (fluoresces) with

Fig. 3.3 A sharp shadow of an obstacle is cast by the cathode rays. The same observation in the case of light rays led to the corpuscular model of light. We recognise today that such an experiment does not prove the particle character; it is only consistent with it. Waves having wavelengths much smaller than the size of the obstacle, also cast sharp shadows. Further investigation reveals that cathode rays (made up of electrons) as well as light rays (made up of photons) have a dual (wave and particle) character.
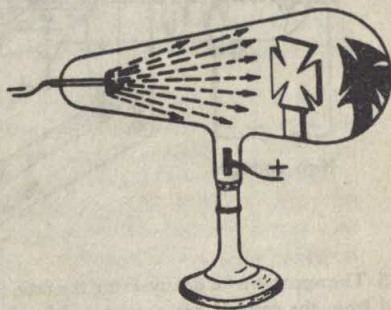
a faint greenish light. It was observed that an object placed inside the tube casts a sharp shadow on the wall of the glass tube (see Fig. 3.3) which now fluoresces only in the region outside the shadow. This experiment showed that the fluorescence is due to the bombardment of the glass by rays emitted from the cathode and moving in straight lines. These rays were named cathode rays for obvious reasons.

3.1.3 Nature of Sub-atomic Constituents

The application of electric and magnetic fields deflected the rays in the discharge tube thus establishing that they consist of charged particles and the direction of deflection showed that the charge is negative (Fig. 3.4). By measuring the deflection under the simultaneous influence of electric

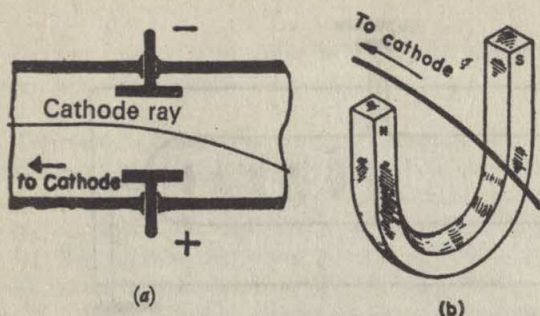*This effect is now widely used in construction of neon signs for display boards.

Fig. 3.4 That cathode rays consist of negatively charged species is shown by the direction of their deflection in these two experiments: (*a*) represents the behaviour in an electric field and (*b*) in a magnetic field.

and magnetic fields, applied perpendicular to each other (as shown in Fig. 3.5), Sir J. J. Thomson (1887) was able to determine the ratio of the charge (e) of the particle to its mass (m). The value of e/m was found to be 1.76×10^8 coulomb/g (5.28×10^{17} esu/g) and the particles were identified as electrons. The ratio e/m was independent of the nature of the gas in the tube as well as the nature of the cathode, thus showing that electrons are universal constituents of all matter.
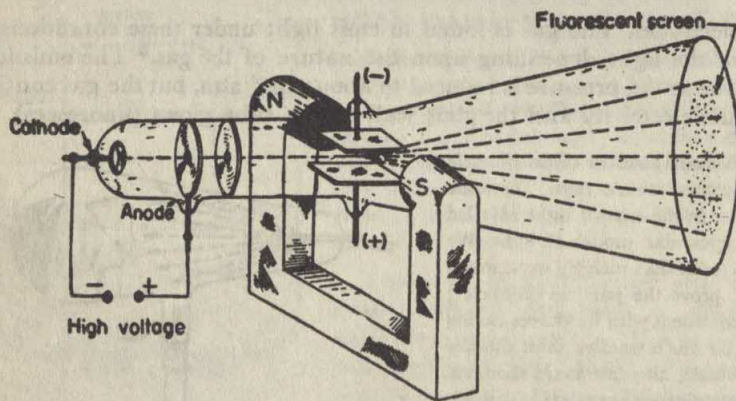

Fig. 3.5 The apparatus for determining the ratio of the charge to the mass of electrons. Electrons emitted from the cathode are accelerated by the high voltage between the cathode and the anode. The circular disc after the anode selects the beam moving in a straight line. The beam then passes through electric and magnetic fields which are perpendicular not only to each other but also to the direction of the motion. Their relative strengths and the ratio e/m controls the deflection. Hence, by measurement of deflection and of field strengths, e/m can be calculated.

The charge of the electron was measured by Millikan in 1909 as 1.60×10^{-19} coulomb (4.8×10^{-10} esu). When combined with the value for e/m, this gives the mass of electron as 9.1×10^{-28} g. Fig. 3.6 depicts the set-up used for determining the charge of an electron.

At moderate pressure, the stream of electrons in a discharge tube collides with the neutral atoms or molecules of the gas producing more electrons as well as other particles which move towards the cathode as rays. The deflection of these rays, called canal rays, in an electric field shows that they consist of positive ions (Fig. 3.7). The charge and mass of the positive ions are deter-
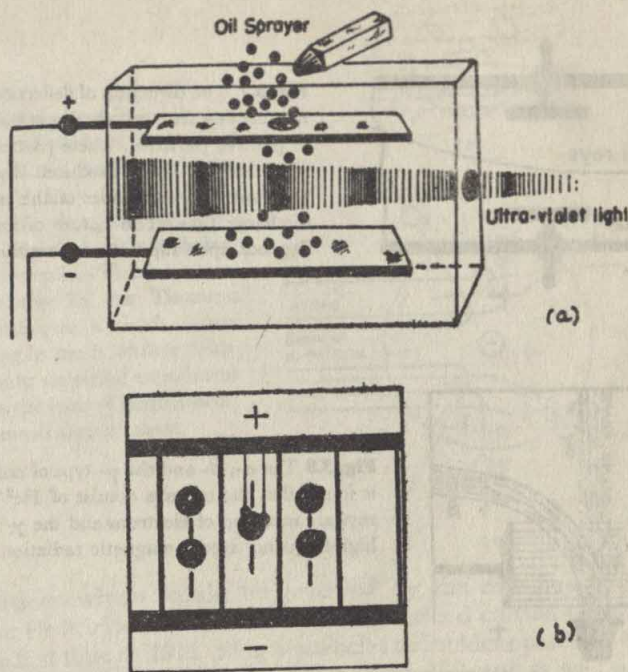
Fig. 3.6 (*a*) Millikan's experiment for determination of charge of electron. Oil drops are sprayed and allowed to fall in between two charged plates. While falling, they are exposed to ultraviolet radiation which ionises the drops.

(*b*) The negatively charged drops experience gravitational field in the downward direction and electric field in the upward direction. By adjusting the electric field strength, the two forces can be balanced. The drop then either remains stationary or moves with constant speed (in accordance with the first law of motion). The charge is calculated by measuring this speed. In this picture one of the oil drops carries two electrons; in an actual experiment the charge on each drop is different. The smallest charge is calculated using a Cannizzaro-type analysis (see Chapter 2).

mined in the same manner as described above. It is found that positive ions are typically about 2,000 times more massive than electrons; their exact mass depending on the nature of the gas in the tube.

The experiments outlined above clearly showed that the atom was not indivisible, but could be split into charged particles. Studies on the phenomenon of radioactivity discovered by Becquerel around 1900, also supported this conclusion. Radioactivity is the spontaneous emission of radiation by certain elements like radium. Three kinds of radiation named a, β and γ have been identified. Their nature has been characterised by methods identical to those used for characterising cathode rays. Alpha rays consist of positively charged He^{2+} particles ($e = 3.20 \times 10^{-19}$ coulomb, $m = 6.6 \times 10^{-24}$ g). Beta rays are made up of electrons, while gamma radiation is high energy electromagnetic radiation having no charge and negligible mass (Fig. 3.8). Radioactivity is discussed in detail in Chapter 19.
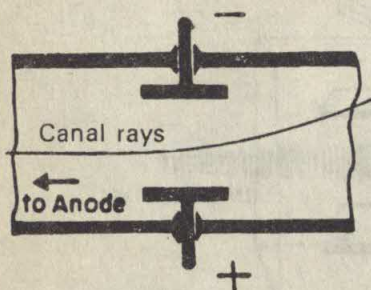
Fig. 3.7 The direction of deflection of the canal rays coming from anode shows that they consist of positive particles. These particles have been identified as ions produced by collison of electrons with molecules of the residual gas in discharge tube. The nature of ions, naturally, depends upon the nature of residual gas.
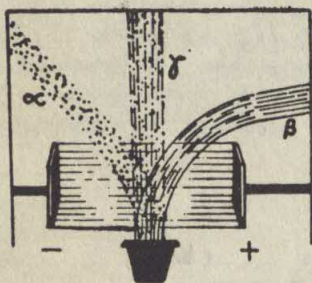
Fig. 3.8 The α-, β- and the γ- type of radioactivity. It is found that the α- rays consist of He^{2+} ions, the β- rays are made up of electrons and the γ- rays are just high-frequency electromagnetic radiation.

3.2 EARLY MODELS OF THE ATOM

The question that had to be answered next was with regard to the arrangement of the constituent particles inside an atom. J. J. Thomson proposed the first model in which the positive charge was assumed to be smeared over a sphere of radius 10^{-8} cm* with the electrons embedded in the sphere (Fig. 3.9). The validity or otherwise of such a model could be tested, by shooting charged particles through thin metal foils and studying the resultant scattering of
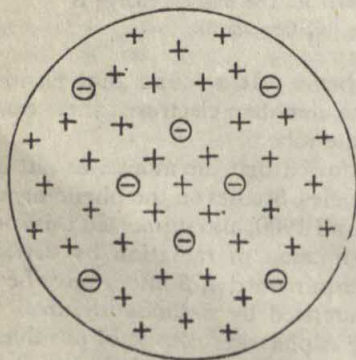

Fig. 3.9 The Thomson model of an atom. The positive charge was imagined as being spread over the entire atom and the electrons were put in this positive background. This model proved inconsistent with experimental facts.

*The approximate value for the atomic radius had been earlier deduced from the kinetic theory of real gases.

Fig. 3.10 (a) Type of results scattering experiments should yield on the basis of Thomson's model. Practically, all of the α-particles would have gone through undeflected or at the most deflected through small angles. A violent deflection would be impossible. This is because the positive charge in the Thomson model is spread over a much larger volume resulting in much weaker fields. (b) Type of results scattering experiment should yield on the basis of Rutherfords' model. Experiments support these.
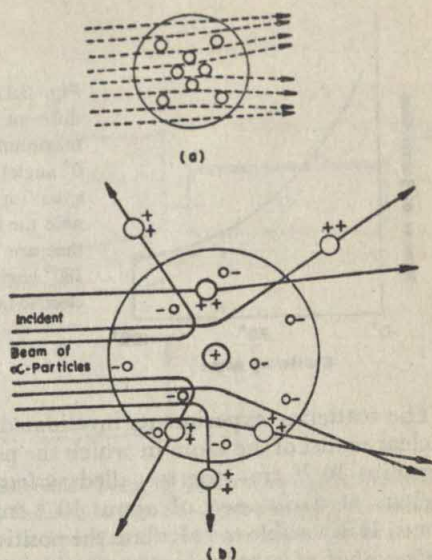
incident particles which would be governed by the distribution of positive and negative electricity inside the atoms. Rutherford carried out this experiment for the first time in 1911 using α-particles as incident particles and a gold foil as the target. The scattered particles were detected as well as counted by the fluorescence they produced on a zinc sulphide screen. It was observed that a majority of the α-particles went through the foil undeflected while only a small fraction was deflected by small angles. The unexpected but crucial feature was that one in about 20,000 particles came straight back suffering a deflection of 180°. Such violent deflection can arise only if there is an intense electric field inside atoms. Calculations showed that positive charge spread over a sphere of radius 10^{-8} cm would be incapable of producing such a field; indeed the radius has to be of the order of 10^{-13} cm to account for the scattering data. Figs. 3.10, 3.11 and 3.12 illustrate the various features of the scattering experiment.
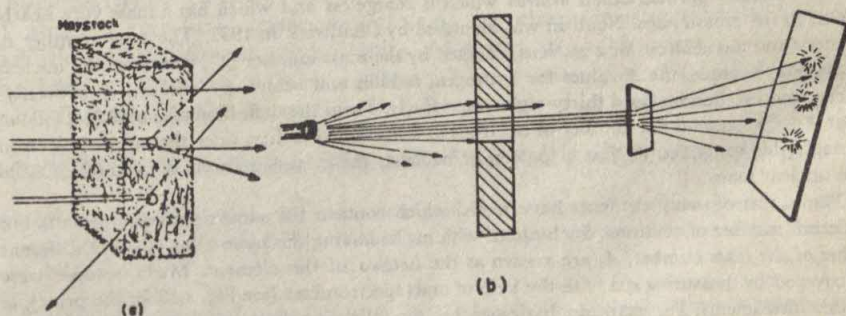
Fig. 3.11 (a) Gold nuggets in a haystack can be located by shooting bullets. The number of bullets that get 'scattered' and the number of bullets that go undeflected can together give a clue to the locations and the sizes of the nuggets. (b) α-particle scattering, in Rutherford's experiment, similarly yields nuclear size.
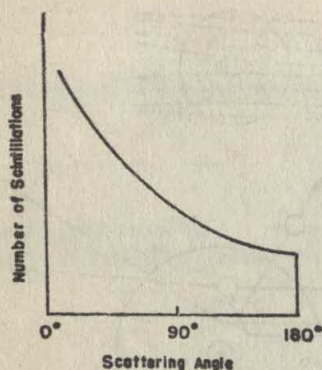
Fig. 3.12 The number of α-particles scattered at different angles as a function of the angle. Note that maximum number are undeflected (i.e. scattered with 0° angle) showing that major portion of atom is empty space (or more correctly space with weak field). Also note the small but not negligible number of particles that are deflected straight back (i.e. scattered with 180° angle). This can only happen if an intense positive electric field exists over a small volume in the atom.

The scattering experiments invalidated the Thomson model and led to the nuclear model of the atom in which the positive charge is spread over a sphere of radius 10^{-13} cm—the so-called *nucleus*—and the electrons are outside the nucleus at a distance of about 10^{-8} cm to account for the typical size of atoms. It is possible to calculate the positive charge on the nucleus by counting the number of α-particles scattered in different directions. In this manner it was found that the charges of different nuclei are always integral multiples of the electron charge but with opposite sign. Thus, if the electron charge is designated as $-e$, the nucleus of hydrogen atom is found to have a charge of $+1e$, the nucleus of sodium atom $+11e$, and that of uranium atom $+92e$. This integer value is called the *atomic number** and denoted by the symbol Z. Furthermore, since atoms are electrically neutral, one has to assume that there are as many electrons in an atom as the net positive charge on the nucleus. This means that the hydrogen atom has one electron, the sodium atom has eleven electrons and the uranium atom has ninety-two electrons.

The positive charge of a nucleus is due to the positively charged particles called *protons*. The proton charge is equal to the electron charge in magnitude, but opposite in sign. This means that the atomic number Z of a nucleus is equal to the number of protons in that nucleus. For example, the nuclei of hydrogen, sodium and uranium atoms have one, eleven and ninety-two protons respectively. But whereas the charge of a nucleus is entirely due to the protons, the mass of a nucleus is not due to the protons alone. This is because of the fact that nuclei contain another particle called *neutron* which is chargeless and which has a mass very nearly equal to the proton mass. Neutron was identified by Chadwick in 1932. The total number of protons and the neutrons in a nucleus, denoted by the mass number (A), determine the nuclear mass. For example, the A values for hydrogen, sodium and uranium nuclei are one, twenty-three, and two hundred and thirty-eight respectively. From the definition of A and Z, it follows that $A - Z$ represents the number of neutrons in a nucleus. Further, since the mass of electron is negligible compared to that of proton or neutron, the mass of an atom is virtually equal to the nuclear mass.

The atoms of many elements have nuclei which contain the same number of protons but different number of neutrons. Such atoms with nuclei having the same value of Z but different value of the mass number, A, are known as the *isotopes* of the element. Many isotopes were discovered by measuring e/m with the help of mass spectrometer (see Fig. 3.13 for the principle of this instrument). For example, hydrogen has the following three isotopes: one isotope with

*The exact determination of atomic number was carried out by Moseley (1915) who studied x-ray scattering (rather than α-particle scattering) from metal targets. Rutherford's experiments could yield only rough estimates of atomic numbers.
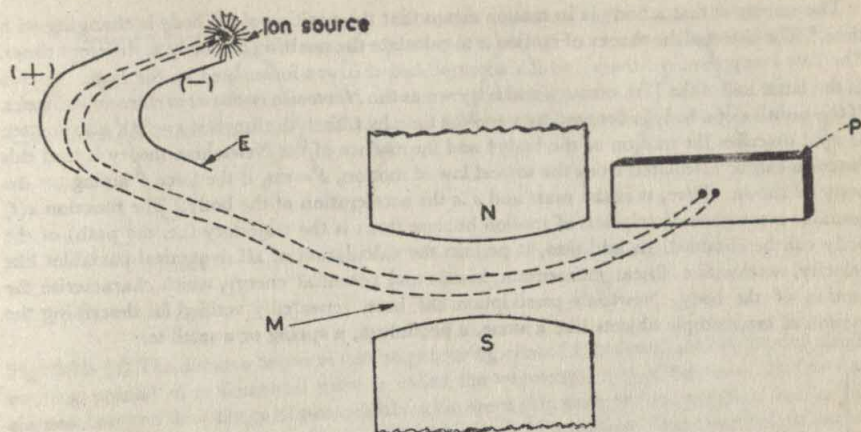
Fig. 3.13 A mass spectrometer is used to determine masses of ions accurately. It essentially measures e/m ratio according to the principles discussed in Fig. 3.5. Since charges of the ions are known, masses can be obtained from the ratio. In the ion source, atoms or molecules are ionised and the ion beams then pass through the electric field E and the magnetic field M. From their location on the detection plate P, masses are calculated. Mass spectrometry, which first revealed the existence of isotopes, is now a powerful tool for analysing molecular structure (see Chapter 4).

$Z=1$, $A=1$ (i.e. one proton only), the second isotope with $Z=1$, $A=2$ (i.e. one proton and one neutron) and the third one with $Z=1$, $A=3$ (i.e. one proton and two neutrons). The term 'hydrogen' is strictly used only for the first isotope while deuterium (symbol D) and tritium (T) refer to the second and the third varieties respectively. The isotopes of other elements do not have special names; they are indicated by giving the A value on the symbol for the elements. Thus, ^{235}U, ^{238}U, ^{239}U, are the isotopes of uranium. Since the properties of the isotopes of an element are similar,* we shall not specifically indicate isotopes in majority of the other chapters of this book. For further discussion of nuclear structure, see Chapter 19.

The Rutherford model of an atom was devised to explain the results of α-particle scattering. But in order to be totally acceptable, it also had to satisfactorily answer questions regarding (*i*) the arrangement of electrons around a nucleus, (*ii*) the cause for stability of this arrangement (i.e. cause for stability of atoms), and (*iii*) *atomic spectra*† (i.e. the characteristic electromagnetic radiation that different atoms emit). Attempts to tackle these problems on the basis of the then well-established *Newton's laws of motion* and *Maxwell's laws of electromagnetism* completely failed as discussed in section 3.5.

## 3.3 CLASSICAL MECHANICS AND ELECTROMAGNETISM

We briefly digress to outline the older theories of motion and of electromagnetism, so that we can appreciate the nature of atomic spectra as well as the reasons for failure of the Rutherford model.

*This is not quite true for the lighter isotopes in which the mass difference is substantial. For example, whereas H_2O is necessary for life, D_2O can destroy it. The ^3He isotope not only shows radically different behaviour (e.g. superfluidity) from ^4He but also from any other known substance!

†A short description of atomic sepectra is given in section 3.4.

The statement that a body is in motion means that the position of the body is changing with time.* The object of the theory of motion is to calculate the position of a body at different times. The first comprehensive theory which accomplished this was formulated by Sir Isaac Newton in the latter half of the 17th century and is known as the *Newtonian mechanics* or *classical mechanics*. If the position of a body is denoted by x and the time by t, then the function $x = f(t)$, also written as $x(t)$, describes the motion of the body† and the essence of the Newtonian theory is that this function can be calculated from the second law of motion, $F = ma$, if the force F acting on the body is known. (Here, m is the mass and a is the acceleration of the body.) The function $x(t)$ contains a complete description of motion because from it the trajectory (i.e. the path) of the body can be obtained. In addition, it permits the calculation of all dynamical variables like velocity, acceleration, linear momentum, kinetic and potential energy, which characterise the motion of the body. Newton's prescription has been repeatedly verified for describing the motion of macroscopic objects like a stone, a pendulum, a spring or a satellite.
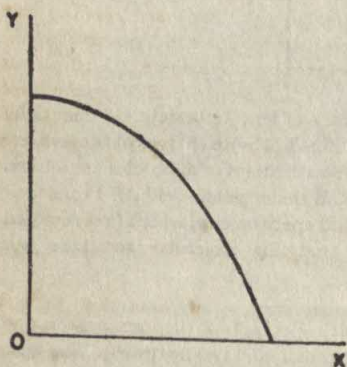
Fig. 3.14 A possible parabolic path a stone would follow when thrown horizontally. The path can be accurately calculated from the Newtonian mechanics. For microscopic objects like electrons, the path of motion cannot be specified for reasons discussed later in this chapter.

A simple illustration can clarify the above ideas. It can be easily verified that if a stone is thrown horizontally, it's path describes a curve known as a parabola (Fig. 3.14). What does Newton's theory say about the motion of the stone? To find the answer, we note that the stone moves under the gravitational force (F) due to the earth. This force, according to the law of universal gravitation, has the form $F = G(m_s m_e / R)$ where G is the gravitational constant, m_s and m_e are the masses of the stone and earth respectively and R is the distance between the two bodies. Substituting this expression in the equation $F = ma$ and solving the resultant differential equation, we get the functions $x(t)$ and $y(t)$ for the stone.‡ Eliminating t provides the function $y(x)$ which turns out to be a parabola, in complete agreement with observed motion.

We shall apply the Newtonian ideas to the Rutherford model in section 3.5. We now turn to a discussion of classical electromagnetism.

The first comprehensive theory of *electromagnetism*, formulated by James Clerk Maxwell in the 1870's successfully describes (at the macroscopic level) the interaction between charged bodies and the behaviour of electric and magnetic fields. This is known as the classical electromagnetic theory. Our concern in this section is with only one aspect of this theory, namely its description of electromagnetic (em) radiation.

*This concept of motion, which seems to be intuitively correct, is found to be (approximately) applicable to macroscopic bodies only. For the quantum concept of ' motion ', see section 3.9.1.

†We are taking the special case of one-dimensional motion. In three dimensions, $x(t)$, $y(t)$, $z(t)$ (where x, y, z are the coordinates specifying the position of a body in space) taken collectively, describe the motion of the body.

‡In this case two coordinates x and y are needed, since the motion is two-dimensional.

Distance ⟶

(a)

Time ⟶

(b)
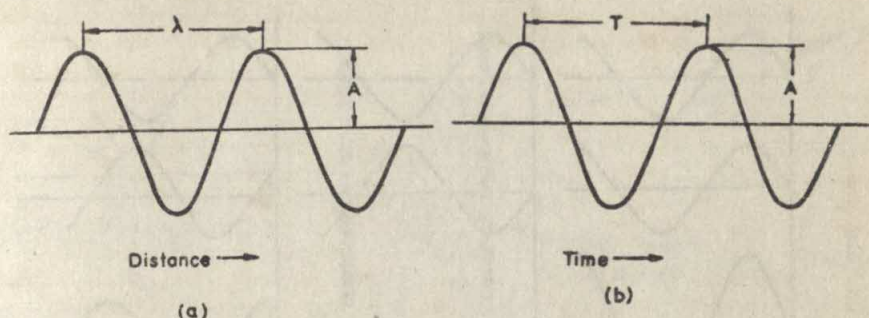
Fig. 3.15 (*a*) The distance between two neighbouring crests (or between any two similar neighbouring points) of a sinusoidal wave is called the wavelength (λ) of the wave. (*b*) The time elapsed between the passage of two neighbouring crests (i.e. time for one complete oscillation) of a sinusoidal wave is called the period (T) of the wave. It is obvious, from these two definitions that the speed, c, of the wave should be given by $\lambda/T = c$. Further, if one complete oscillation takes place in time T, then the number of oscillations, (ν), per unit time is given by $\nu = 1/T$. Combining the two relations, we have $\lambda\nu = c$, a very useful equation in wave phenomena.

' Light ' is the oldest form of radiation known and speculation about its nature dates from remote antiquity. After initial attempts to explain light as made up of particles (corpuscules), the wave theory was established in the 19th century.

To appreciate the arguments which led to the wave theory of light, it is necessary to look briefly into the nature of wave phenomenon. We are all familiar with water waves which exist in oceans and rivers and sound waves which propogate through air. Waves have a variety of shapes, but we shall consider only a particular kind of wave known as a sinusoidal wave.

A sinusoidal wave is characterised by wavelength (λ), period (T), frequency (ν), amplitude (A), and speed of propagation (c). Here λ is the distance between two nearest identical points (e.g. the distance between two neighbouring crests as in Fig. 3.15*a*); T the time between the passing of two neighbouring crests (Fig. 3.15*b*); ν the number of crests that pass a given point per second; A the maximum displacement; and c the distance travelled by a crest per second. The following two relations can be easily deduced from these definitions

$$\nu = 1/T \quad c = \lambda/T = \lambda\nu$$

The energy transported by a wave is proportional to its intensity which in turn is proportional to the square of the amplitude. That is,

wave energy ∝ wave intensity ∝ A^2

When two waves occur together, their superimposition gives the resultant wave. If the two waves have the same frequency and if they attain maximum amplitude at the same place at the same time, they are said to be in phase with each other. On the other hand if the positive maximum amplitude of one wave coincides with the negative maximum amplitude, the waves are said to be out of phase. In between these extremes there are intermediate situations where the waves are neither in phase nor out of phase. It is obvious that the amplitude, and hence the intensity, of the resultant wave depends upon the relative phase difference. These aspects are illustrated in Fig. 3.16. The variation of intensity due to superimposition of waves is known as *interference or diffraction.** Our conclusions can be easily generalised to the interaction between more than two waves.

Interference and diffraction effects (Fig. 3.17) are a crucial test of wave character. They

*There is no important physical difference between interference and diffraction. It seems that the term interference is used when only two waves are interacting while the term diffraction is used for interaction of several waves.
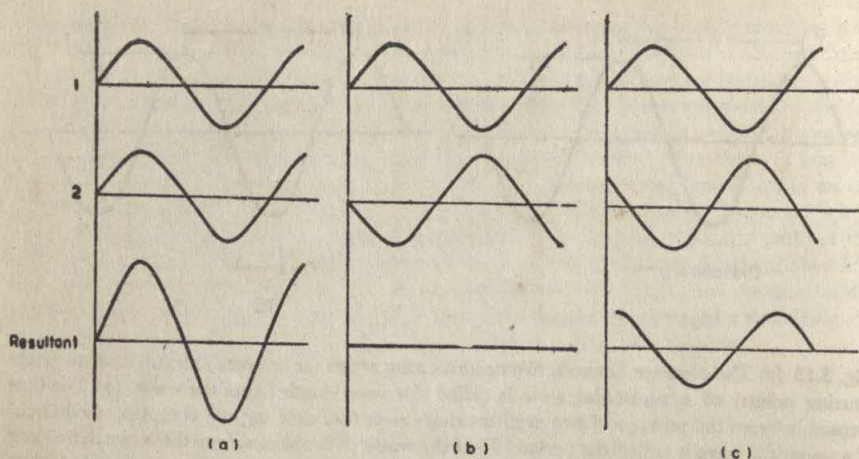
Fig. 3.16 Superposition of two waves having the same frequency and the same amplitude. In (a), the waves are in phase. Hence, they add everywhere leading to a wave of twice the amplitude but the same frequency. In (b) the waves are exactly out of phase and hence they cancel each other. (For light waves such cancellation means light+light=dark!) (c) An intermediate situation where reinforcement takes place in some parts and cancellation in others.

are exhibited when waves encounter an obstacle such that the wavelength is comparable to the size of the obstacle. When experiments involving passage of light beams through pinholes and fine slits were carried out in the early 19th century, diffraction patterns were obtained. This conclusively proved the wave nature of light. The analysis of these patterns also yielded the wavelength. Under ordinary conditions like reflection from a mirror, interference of light is not observed because the wavelength is too small compared to the size of the obstacle.

The electromagnetic (em) nature of light waves was revealed by Maxwell who showed that they consist of oscillating electric and magnetic fields. In addition to light which is the visible form of radiation, other forms of invisible radiation, like ultraviolet radiation, and heat (infrared) radiation, exist which also have electromagnetic nature. In all forms of em radiation, the direction of propagation, the direction of electric field and the direction of magnetic field are perpendicular to each other (Fig. 3.18). It turns out that in vacuum, the speed of propagation, c, of all radiation is constant and equal to 3×10^{10} cm/s. The various forms of em radiation differ only in their frequencies and the various frequency regions are identified by special names. These regions, summarised in Table 3.1, are collectively said to constitute the *electromagnetic spectrum*.

If *frequency* (ν) of radiation is known, its *wavelength* (λ) can be easily calculated from the relation $\lambda\nu = c$. Sometimes it is convenient to specify em radiation in terms of another unit called *wave number* ($\bar{\nu}$) which is related to λ or ν by the relations $\bar{\nu} = 1/\lambda$, or $\bar{\nu} = \nu/c$.

Example 3.1 The frequency of light in the violet region is 7×10^{14} cycles per second (cps). Calculate the corresponding wavelength and the wavenumber.

Rearranging the equation $\lambda\nu = c$ we get,

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^{10}}{7 \times 10^{14}} \text{ cm or } \lambda = 0.4285 \times 10^{-4} \text{ cm} = 4285 \overset{\circ}{A} \quad (1A = 1 \text{ Angstrom} = 10^{-8} \text{cm})$$

Electromagnetic waves have two amplitudes, one denoted by E, for the oscillating electric field, and the other denoted by H, for the oscillating magnetic field. Maxwell's theory shows that the energy contained in an em wave is proportional to the sum of the squares of the electric field amplitude and the magnetic field amplitude. Hence it follows that radiation

(a)

(b)
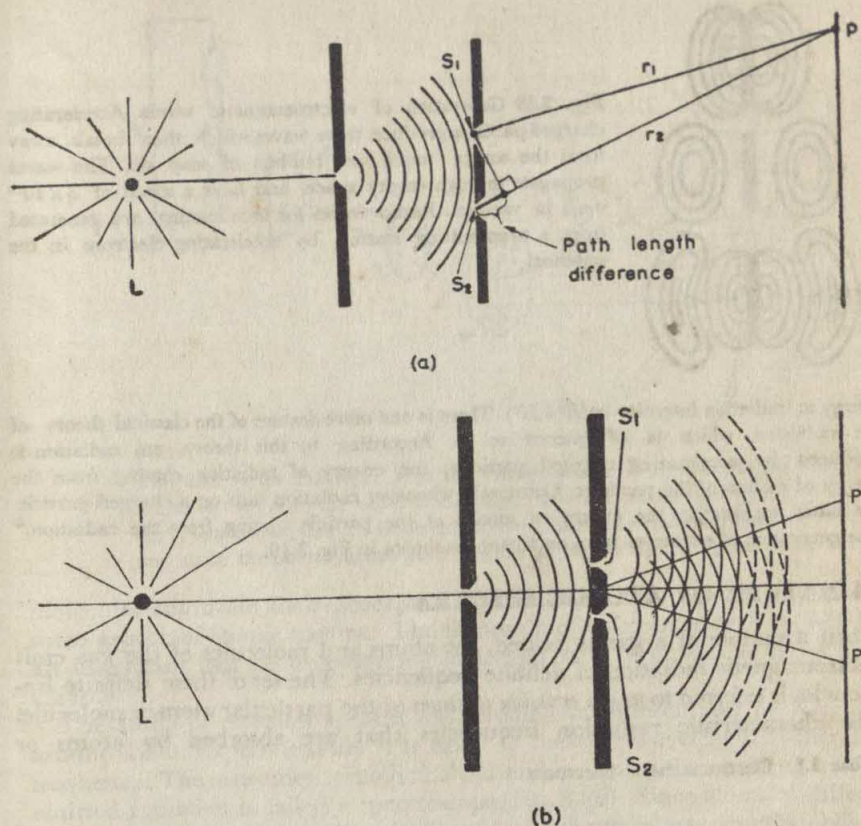
Fig. 3.17 A two-slit interference pattern. In (a) waves from the source L are collimated by the first screen and then pass through the two slits s_1 and s_2 in the second screen. Secondary waves are generated from the slits which interfere with each other. The phase difference between the two wavetrains varies in different directions depending upon the path length difference. In (b) is shown one direction where the path length difference is such that the waves are in phase in this direction. Consequently, maximum intensity is observed at P. The interference of x-rays and electron waves is widely used for molecular and crystal structure determination (see Chapter 4). The mathematical relation between wavelength and path length difference which determines the intensity variation is also derived in Chapter 4.

Fig. 3.18 An electromagnetic wave. The electric field (E) is varying in the xz-plane while the magnetic field (H) is oscillating in the yz-plane. The direction of propagation is along z-plane.
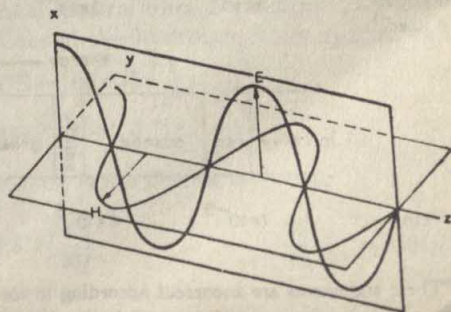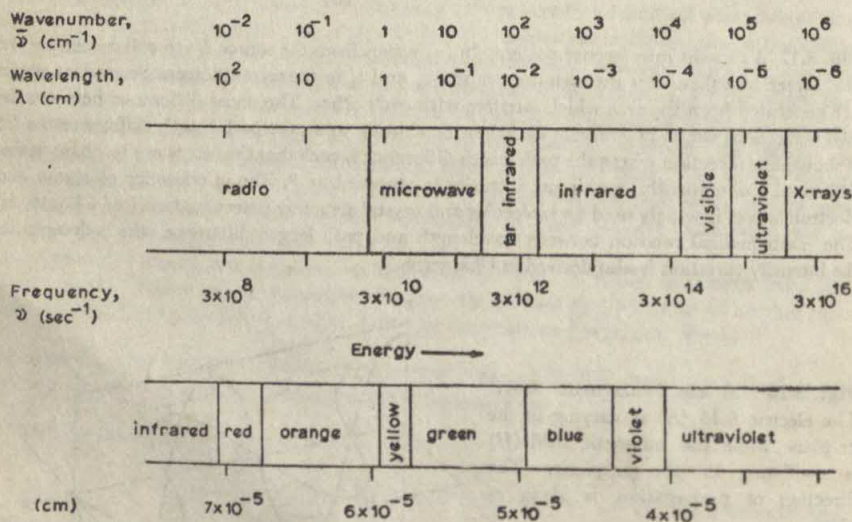
Fig. 3.19 Generation of electromagnetic waves. Accelerating charged particles produce these waves which then break away from the source much like bubbles of soap do. The waves propagate through empty space and have a speed of 3×10^{10} cm/s in vacuum. Radio waves for broadcasting are generated from a transmitting station by accelerating electrons in the antenna.

energy $\propto$ radiation intensity $\propto (E^2 + H^2)$. There is one more feature of the classical theory of the radiation which is of interest to us. According to this theory, em radiation is produced by accelerating charged particles; the energy of radiation coming from the energy of motion of the particles. Conversely, whenever radiation falls on a charged particle, the latter accelerates; the energy of motion of the particle coming from the radiation.[*] The generation of em waves from an antenna is shown in Fig. 3.19.

3.4 NATURE OF ATOMIC SPECTRA

When a sample of a gas is heated, the atoms and molecules of the gas emit electromagnetic radiation of definite frequencies. The set of these definite frequencies is referred to as an *emission spectrum* of the particular atom or molecule. The characteristic radiation frequencies that are absorbed by atoms or

Table 3.1 Electromagnetic Spectrum

Wavenumber, $\bar{\nu}$ (cm^{-1})	10^{-2}	10^{-1}	1	10	10^2	10^3	10^4	10^5	10^6
Wavelength, λ (cm)	10^2	10	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}

| | radio | microwave | far infrared | infrared | visible | ultraviolet | X-rays |

| Frequency, ν (sec^{-1}) | 3×10^8 | | 3×10^{10} | | 3×10^{12} | | 3×10^{14} | | 3×10^{16} |

Energy ⟶

| infrared | red | orange | yellow | green | blue | violet | ultraviolet |

| (cm) | 7×10^{-5} | 6×10^{-5} | 5×10^{-5} | 4×10^{-5} |

[*]These statements are incorrect according to the quantum theory which suggests an alternate mechanism for generating em radiation, see section 3.7.
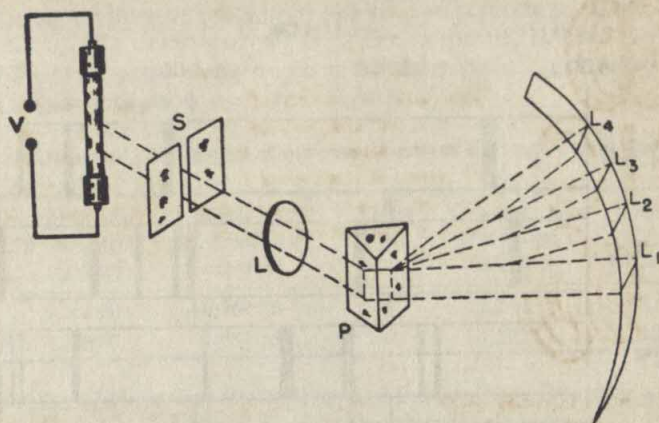
Fig. 3.20 A spectroscope. V is the voltage source used to excite the atoms of the gas in the tube. The emitted radiation passes through the slit S, lens L and prism P. Different wavelengths bend to different extents and strike the photographic plate at different points L_1, L_2, L_3 and L_4.

molecules constitute their absorption spectra. We shall now briefly discuss some aspects of atomic spectra. The discussion of *molecular spectroscopy*, which is an important tool for investigating molecular structure, will be taken up in Chapter 4.

The study of emission spectra was initiated by Bunsen and by Kirchhoff around 1860. Experimentally it is easier to measure wavelength, rather than frequency. The instrument which analyses and measures the wavelength of the emitted radiation is called a spectroscope (Fig. 3.20). Since atoms of different elements were found to emit radiations of unique sets of wavelengths, emission spectra became useful in chemical analysis to identify and estimate the elements present in a sample* even before the origin and the nature of spectra was understood.

The most striking feature of *atomic spectra* is that the emitted (or absorbed) radiation has very sharp, discrete wavelengths. These spectra are, therefore, also known as line spectra. The spectra of some typical atoms are shown in • Fig. 3.21. As can be seen, the hydrogen atom (which contains only one electron) gives by far the simplest pattern. Considerable effort was expended in the early days to find some regularity amongst the wavelengths given out by this atom. Finally, Balmer showed in 1885 that if spectral lines are expressed in terms of wave number, $\bar{\nu}$, then the visible lines of the hydrogen atom spectra can be fitted to the formula, $\bar{\nu}$ (in cm^{-1}) $= 109{,}677 \left(\dfrac{1}{2^2} - \dfrac{1}{n^2} \right)$
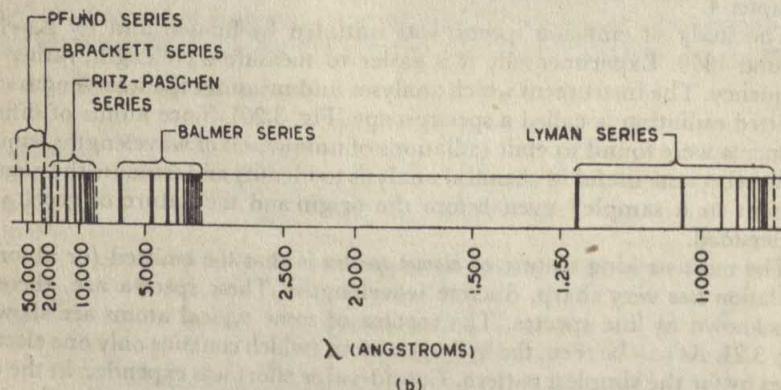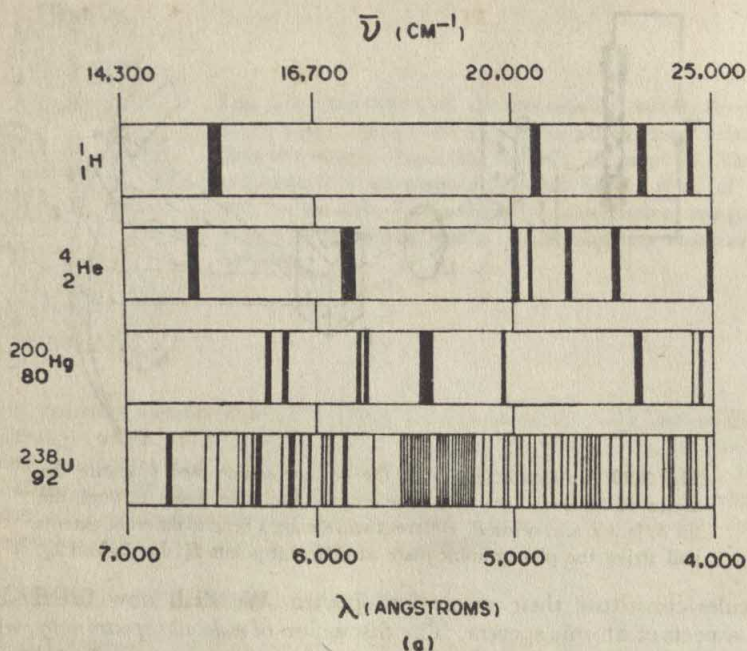
where n is an integer equal to or greater than 3 (i.e. $n = 3, 4, 5, \ldots$).

Example 3.2 Calculate the wavelength from the Balmer formula when $n=3$.

$$\bar{\nu} \ (cm^{-1}) = 109{,}677 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 109{,}677 \left(\frac{5}{36} \right) \qquad \lambda = \frac{1}{\nu} = \frac{36}{5 \times 109{,}677} = 6564 \cdot 73 \ A$$

*The elements rubidium and cesium were discovered using this tool.

$$\bar{\nu} \ (\text{CM}^{-1})$$

14.300   16.700   20.000   25.000

$^1_1$H

$^4_2$He

$^{200}_{80}$Hg

$^{238}_{92}$U

7.000   6.000   5.000   4.000

λ (ANGSTROMS)

(a)

┌PFUND SERIES
┌BRACKETT SERIES
┌RITZ-PASCHEN
 SERIES
┌BALMER SERIES   ┌LYMAN SERIES┐

50,000 20,000 10,000 5,000   2,500 2,000 1,500 1,250   1,000

λ (ANGSTROMS)

(b)

Fig. 3.21 (*a*) The spectra in the visible region of some atoms. The particular isotopes have been indicated since the wavelengths of the emitted lines depend to some extent on the mass of the nucleus. (*b*) The complete spectrum of the hydrogen atom. The positions of all the lines are accurately predicted by the Rydberg formula given in the text.

The calculated wavelength from the Balmer formula for a few values of *n* are given in Table 3.2. Note the close agreement with the experimental values obtained from analysis of the visible region of the hydrogen atom spectrum (Fig. 3.21*b*). Soon after Balmer, Rydberg showed that the more general expression,

$$\bar{\nu}(\text{in cm}^{-1}) = 109{,}677 \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

where n_1 and n_2 are integers (such that $n_1 > n_2$), can reproduce all the observed spectral lines of the hydrogen atom. The constant 109,677 which has the dimension of reciprocal length and is characteristic of the hydrogen atom, is called the *Rydberg constant*.

Table 3.2 Comparison of Calculated and Measured Values of Hydrogen Atom Spectra

Value of n	Computed values of wavelength (Angstrom)	Measured values of wavelength (Angstrom)	Value of n	Computed values of wavelength (Angstrom)	Measured values of wavelength (Angstrom)
3	6,562·08	6,562·85	5	4,340·10	4,340·47
4	4,860·80	4,861·33	6	4,101·20	4,101·47

It is, of course, obvious that the Balmer and the Rydberg formulae are purely empirical. They only highlighted the fact that the wavelengths in the hydrogen atom spectra are not random numbers but that they are connected by a simple mathematical relation. However, it was expected of a satisfactory model of atomic structure to provide a rationale for these formulae. We discuss in the next section how the Rutherford model fared in this respect.

3.5 FAILURE OF THE RUTHERFORD MODEL

As stated earlier, Rutherford established, on the basis of the scattering experiments, that an atom consists of a heavy positively charged nucleus (radius $\approx 10^{-13}$ cm) with lighter negatively charged electrons moving outside over an approximate radius of 10^{-8} cm. This model of the atom bears a strong resemblance to the solar system with the nucleus playing the role of the massive sun and the electrons being similar to the lighter planets. Furthermore the *coulomb force* ($= q_1 q_2 / r^2$, where q_1 and q_2 are the charges and r is the distance of separation of the charges) between an electron and the nucleus is mathematically similar to the gravitational force between a planet and the sun. When Newtonian theory was applied to the solar system, it showed that the planets describe well-defined orbits around the sun which persist forever. The theory could also precisely calculate the orbits and these were in impressive agreement with experimental measurements. The similarity between the solar system and the nuclear model makes it obvious that according to classical mechanics, electrons should move around the nucleus in well-defined calculable orbits. However, there arises a difficulty. In describing an orbit, a body undergoes acceleration.[*] So an electron, describing planet-like orbits would accelerate and the electromagnetic theory demands that charged particles when accelerated should emit electromagnetic radiation. (This difficulty does not exist for planets since they are uncharged.) Therefore, an electron in orbit will emit radiation; the energy carried by radiation coming from electron motion. The orbit will thus continue to shrink[†] until the electron falls into the nucleus as shown in Fig. 3.22. Thus,

---

[*]Remember that acceleration is the rate of change of velocity, and both acceleration and velocity are vector quantities (i.e. they have magnitude as well as direction). In an orbit, the direction is continuously changing. Therefore, even if a body is moving with constant speed in an orbit, it must accelerate because of changing direction.

[†]Calculations show that it should take an electron only 10^{-8}s to spiral into the nucleus.

the Rutherford model cannot explain the stability of the atom if the motion of the electron is described on the basis of Newton's laws of motion and electromagnetic theory. Since the latter also predicts that the frequency of radiation of a charged body is equal to the frequency of revolution, it follows that as the

Fig. 3.22 Had an electron followed the classical laws of motion and electromagnetism, it would continuously radiate energy because of acceleration. It would, consequently, spiral into the nucleus. Since this is not observed, it follows that the classical laws cannot be used to describe electron motion.

electron orbit continuously changes so would its frequency of revolution. The atomic spectra should have been, therefore, continuous rather than discrete, in sharp contradiction to the observed facts. The essence of the problem can then be summarised as follows. Scattering experiments require a nuclear atom, but if electron motion is calculated using Newtonian laws and electromagnetic theory, then the Rutherford atom can neither have stability nor exhibit line spectra.

3.6 DUAL NATURE OF RADIATION: FAILURE OF CLASSICAL ELECTROMAGNETIC THEORY

Even before the Rutherford model, evidence had been accumulating to show the inability of the classical theory of radiation to account for several experimental observations. Two principal phenomena where the wave theory failed are discussed below.

It is a common experience that when an object is heated its colour gradually changes. For example, black coal becomes red, orange, blue and finally 'white hot' with rising temperature. This means that the 'red' radiation is most intense at a particular temperature, 'blue' radiation is most intense at another temperature and so on. In other words, the intensities of radiation of different wavelengths emitted by a hot body depend upon its temperature. It is possible to experimentally determine the intensity or energy distribution as a function of wavelength at various temperatures. Some typical curves obtained for a black-body (which is generally used because it is a perfect emitter of radiation) are shown in Fig. 3.23. All attempts to explain such curves on the basis of the wave theory of radiation were unsuccessful.

Fig. 3.23 The observed intensity of radiation for different wavelengths emitted by a black-body at 1500 K and 2000 K. The maximum shifts towards lower wavelength with increase in temperature. The predicted curve for 1500 K according to the classical theory is completely at variance with the observations. Planck's theory, however, successfully reproduced experimental curves.
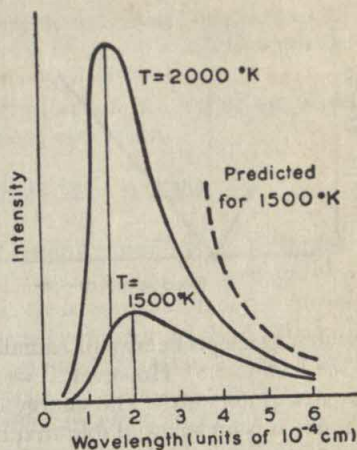
Max Planck, in 1900, showed that the observed energy distribution can be obtained if it is assumed that the hot body emits or absorbs radiation energy in the form of bullets of energy. These corpuscles or quanta of light were later named *photons*. Planck's assumption implies that the absorption or emission process is discontinuous (quantised) rather than continuous as the wave theory postulates. From an analysis of the data it was found that the amount of radiant energy (E) in a photon is proportional to the frequency (ν) of the radiation:

$$E \propto \nu$$
$$\text{or } E = h\nu$$

where h, the constant of proportionality known as the *Planck's constant*, has the measured value of 6.6252×10^{-27} erg.s. Planck's constant is one of the fundamental constants of nature and it is the cornerstone of the modern theory of radiation and matter.

Example 3.3 Wavelength of light in the yellow region is 5890 A. Calculate the energy in one photon of yellow light.

The energy, E, of one photon is $E = h\nu$. Combining this with $\lambda\nu = c$,

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-27} \text{ erg.s})(3.00 \times 10^{10} \text{cm/s})}{5890 \times 10^{-8} \text{ cm}}$$
$$= 3.37 \times 10^{-12} \text{ erg}$$

Planck's assumption of quantisation was restricted to the absorption and emission of radiation, but Einstein (in 1905) showed that if it is assumed that radiation also propagates in the form of photons, then it was very easy to explain the *photoelectric effect*. When a clean metallic surface in vacuum is irradiated with monochromatic light, electrons are emitted from the metal. It is found that the kinetic energy of the emitted electrons (*photoelectrons*) increases linearly with the frequency of the incident light (Fig. 3.24). If the frequency is decreased below a critical value (called threshold frequency, ν_0) no emission is observed. The ν_0 value is of characteristic of the metal used. It is also observed that increasing the intensity of radiation has no effect on the energy of photoelectrons; it merely increases their number. This effect discovered by Heinrich Hertz in 1887 is incomprehensible on the basis of the wave theory
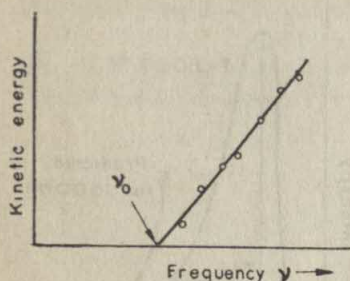
Fig. 3.24 The kinetic energy of electrons emitted in a photoelectric effect experiment, as a function of frequency of incident radiation. For a particular metal, there is a lowest frequency (threshold frequency) below which electrons are not emitted (i.e. kinetic energy is zero). In the figure ν_0 is the threshold frequency.

which connects energy of radiation with intensity rather than with frequency (see section 3.3). However, if we accept the photon hypothesis, the explanation is straightforward. The energy of a photon is proportional to frequency and hence it is understandable that the energy of the photoelectrons increases with the frequency of the incident light. Further, the intensity of the radiation is proportional to the number of photons. So the number of photoelectrons should increase when the intensity is increased.

When a photon strikes the metallic surface, it gives up its energy to the electron. Part of this energy (say W) is used by the electron to escape from the metal, the remaining shows up as the kinetic energy ($\frac{1}{2}mv^2$) of the photoelectrons. If the incident radiation has frequency ν, then its photons have energy $h\nu$, and it follows from the conservation of energy principle that,

$$h\nu = \tfrac{1}{2}mv^2 + W$$
$$\text{(or) } \tfrac{1}{2}mv^2 = h\nu - W$$

This equation shows that if the kinetic energy is plotted against the frequency of the incident light, a straight line should be obtained in agreement with the observations. Also, the slope of the line was found to be equal to the Planck's constant as demanded by the above equation.

Example 3.4 The threshold wavelength (λ_0) of sodium metal is 6500 A. If uv light of wavelength 360 A is used, what will be the kinetic energy of the photoelectrons?

The threshold frequency (ν) corresponding to the wavelength 6500 A is c/λ_0.
Therefore, the threshold energy $= h\nu_0 = hc/\lambda_0$
Substituting for h, c and λ_0 we get,
    threshold energy $= 3 \cdot 056 \times 10^{-12}$ erg
The energy of the incident photons is given by
    $h\nu = hc/\lambda$
Since the incident wavelength $\lambda = 360$ A, the incident energy $= 55.175 \times 10^{-12}$ erg
The kinetic energy (KE) of the photoelectrons will be the difference of incident energy and threshold energy.
    $\therefore$ KE $= h\nu - h\nu_0$
        $= (55 \cdot 175 \times 10^{-12}) - (3 \cdot 056 \times 10^{-12})$ erg
        $= 52 \cdot 119 \times 10^{-12}$ erg

The black-body problem and the photoelectric effect conclusively showed that radiation has corpuscular (particle) character. However, the wave nature cannot be ignored because the interference and diffraction effects of radiation cannot be understood from the particle picture. Thus, the dual nature of radiation is an experimental fact and Maxwell's theory is inadequate as it describes only the wave aspect of the radiation.

The search for a new electromagnetic theory led to quantum electro-dynamics, which takes the dual nature of radiation into account in a consistent manner. However, for most chemical

phenomena, a detailed understanding of the principles of the new theory is not required. The particle character is sufficient to understand photoelectric effect or photochemical reactions, while the wave character is invoked for phenomena like x-ray diffraction.

It was amidst this background, that the next important step in the theory of atomic structure, discussed in the next section, was taken.

3.7 THE BOHR MODEL OF THE HYDROGEN ATOM

Niels Bohr (1913) showed a way out of the dilemma posed by the Rutherford model. He reasoned that the nuclear model of the atom must be accepted since it was based on experiment. Next, since atoms are known not to collapse, Bohr decided to explore the idea that there are special electron orbits in which the electron, in spite of accelerated motion, does not emit radiation.* Since a body has definite energy and angular momentum in a particular orbit, the assumption of special orbits is equivalent to assuming that an electron in an atom has special energies and angular momenta. Formulating these ideas mathematically for the hydrogen atom, Bohr found it necessary to assume that stable (circular) orbits are those in which the *electronic angular momenta* (mvr) are given by $mvr = nh/2\pi$ where n, called the *principal quantum number*, is any integer (i.e. $n = 1, 2, 3$). This condition, known as the quantum condition, leads to the fact that electronic energy can have only discrete, and not continuous, values. It can be shown that the permitted values of energy (E_n), of orbit radii (r_n) and of electronic velocities (v_n) are given by the expressions $E_n = -2\pi^2 me^4/n^2h^2$, $r_n = n^2h^2/4\pi^2me^2$ and $v_n = 2\pi e^2/nh$ where m and e are the mass and charge of the electron and n is the principal quantum number. Numerical calculations using these equations are illustrated in Examples 3.5–3.10.

The main steps in Bohr's theory are as follows. Consider the electron (charge $-e$, mass m) in the hydrogen atom to be moving in a circular orbit of radius r around the nucleus (charge $+e$) as shown in Fig. 3.25. The velocity v of the electron at each instant is tangent to the circular orbit and hence, as the electron proceeds around the circle, the velocity (direction only) changes. This change in the velocity results in the acceleration (a) which is directed towards the nucleus. The magnitude of the acceleration can be calculated from the geometry of the figure to be v^2/r. The force causing this acceleration is the attractive coulomb force $(= e^2/r^2)$ between the nucleus and the electron. Substituting the magnitudes of the force and the acceleration in the equation $F = ma$, we get

$$e^2/r^2 = mv^2/r \tag{1}$$

or, multiplying by r,

$$e^2/r = mv^2 \tag{2}$$

Fig. 3.25 An electron (charge $-e$) describing a circle of radius r around a nucleus (charge $+e$). The velocity at every point on the circle is perpendicular to the radius while the acceleration (not shown in the figure) is parallel to the radius but directed towards the nucleus.
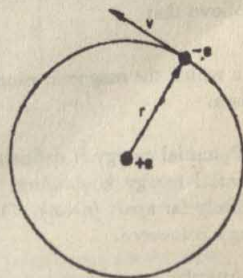
*This idea was invoked in order to explain the stability of the atom.

The total energy, E, of the electron is equal to the sum of the kinetic energy ($\frac{1}{2}mv^2$) and the potential energy ($-e^2/r$).[*]

$$E = (1/2)mv^2 - (e^2/r) \qquad (3)$$

From (3) and (2), it follows that

$$E = \frac{e^2}{2r} - \frac{e^2}{r} = -\frac{e^2}{2r} \qquad (4)$$

If we continue further on the basis of the classical theories, the radius r should keep on decreasing, leading to continuous spectra and an unstable atom. Bohr at this stage, therefore, introduced the novel assumption of stationary orbits. In these orbits, the magnitude of the angular momentum[†] ($L = mvr$) of the electron is an integral multiple of $h/2\pi$, and under this condition, the electron does not emit radiation. This restriction, known as the *quantum condition*, is expressed by the equation

$$L = mvr = nh/2\pi \qquad (5)$$

where n, called the *principal quantum number*, is a non-zero positive integer; i.e. $n = 1, 2, 3,...$ (all integers to ∞). This means that only those orbits which fulfil condition (5) are stable and, therefore, these are the only permissible orbits for the electron in the hydrogen atom. To obtain the expression for the permitted radii (r_n), we substitute the value of $v = nh/2\pi mr$ from (5) into equation (2).

$$\frac{e^2}{r} = \frac{mn^2h^2}{4\pi^2m^2r} = \frac{n^2h^2}{4\pi^2mr^2} \qquad (6)$$

On rearrangement, this becomes

$$r_n = \frac{n^2h^2}{4\pi^2me^2} \qquad (7)$$

Equations (7) and (4) lead to the permitted energies (E_n) given by,

$$E_n = -2\pi^2me^4/n^2h^2 \qquad (8)$$

while (7) and (5) yield the permitted velocities (v_n) as

$$v_n = 2\pi e^2/nh \qquad (9)$$

Similarly other dynamical quantities like linear momentum and kinetic energy can be calculated for any permitted orbit using the above equation. Fig. 3.26 shows the picture of the hydrogen atom based on the Bohr model.

A quantity of considerable importance in chemical applications is the *magnetic moment*. The expression for the magnetic moment of the hydrogen atom is derivable from the Bohr theory in the following manner. If an electric current I travels through a circular wire of radius r, then the magnetic moment, μ, at distances larger than the size of the ring is given by, $\mu = \pi Ir^2/c$. An electron moving in one of the circular orbits of Bohr is equivalent to a circular current. In a particular orbit, the electron passes a given point $v/2\pi r$ times per second. Therefore, the current I, which is the total charge passing a point per second, is $I = ev/2\pi r$, or $\mu = evr/2c$. Since $L = mvr$, it follows that

$$\mu = eL/2mc \qquad (10)$$

from which the magnetic moment in any orbit can be calculated since the values of L are known.

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[*]Potential energy is defined only with respect to a standard state. This particular form of potential energy is obtained by assigning zero value when the nucleus and the electron are infinitely far apart ($r = \infty$). The negative sign indicates that for shorter distances the potential energy is lowered.

[†]Angular momentum is a vector quantity, the direction being perpendicular to the plane of the orbit. Bohr's assumption referred to only magnitude. The quantisation of direction was introduced later. See section 3.10.1.
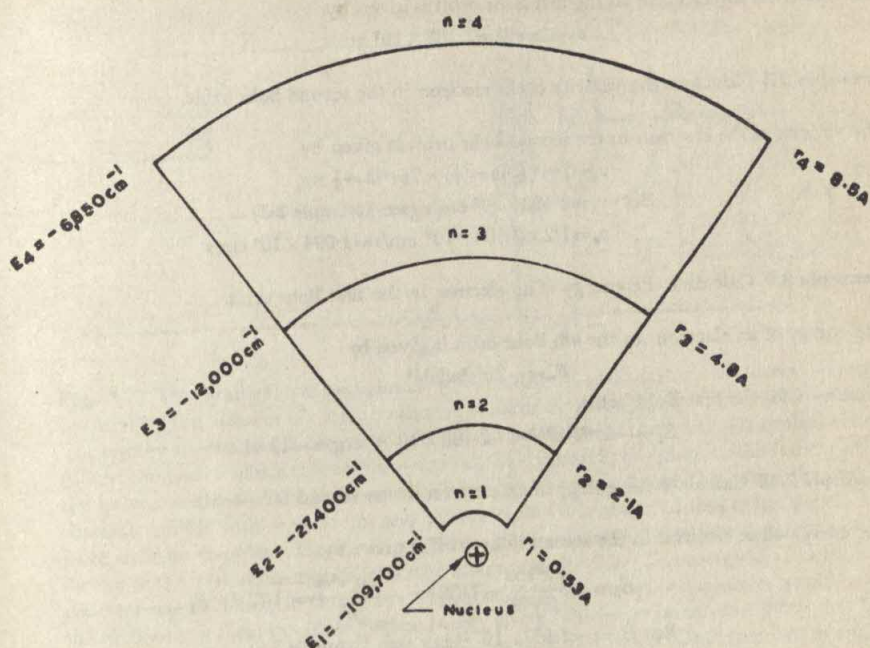
Fig. 3.26 The radii and energies of various permitted orbits in Bohr's model of hydrogen atom. In each of these orbits, the angular momentum is the given value of n multiplied by $h/2\pi$. The smallest value of the angular momentum is in the orbit closest to the nucleus. This orbit is called the ground state because electron energy is also lowest in this state. The energies have negative values since the zero of energy is defined as that state where electron is at infinite distance from the nucleus.

Example 3.5 Calculate the radius of the first Bohr orbit.

The Bohr orbit radii are given by the formula $r_n = n^2 h^2 / 4\pi^2 m e^2$. For the ground state, $n=1$. Therefore the radius (r_1) of the ground state orbit is $r_1 = h^2 / 4\pi^2 m e^2$. Substituting the values of h, π, m and e, we get

$$r_1 = 0.529 \times 10^{-8} \text{ cm} = 0.529 \text{ A}$$

Example 3.6 Calculate the radius of the second Bohr orbit.

The radius of the second Bohr orbit $(r_2, n=2)$ is given by

$$r_2 = \frac{(2)^2 h^2}{4\pi^2 m e^2} = (2)^2 \times \frac{h^2}{4\pi^2 m e^2} = (2)^2 \times r_1$$

But $r_1 = 0.529 \text{ A}$ (see Example 3.5)

$$\therefore r_2 = 4.0 \times 0.529 \times 10^{-8} \text{ cm}$$
$$= 2.116 \times 10^{-8} \text{ cm} = 2.116 \text{ A}$$

Example 3.7 Calculate the velocity of the electron in the first Bohr orbit.

The velocity of the electron in the nth Bohr orbit is given by $v_n = nh/2\pi m r$ where $r = n^2 h^2 / 4\pi^2 m e^2$. Substituting for r in the expression for velocity we get

$$v_n = \frac{nh}{2\pi m} \times \frac{4\pi^2 m e^2}{n^2 h^2} = \frac{2\pi e^2}{nh}$$

The velocity of the electron in the first Bohr orbit is given by

$$v_1 = 2\pi e^2/h = 2 \cdot 188 \times 10^8 \text{ cm/s}$$

Example 3.8 Calculate the velocity of the electron in the second Bohr orbit.

The velocity of the electron in the second Bohr orbit is given by

$$v_2 = 2\pi e^2/(2)h = (\tfrac{1}{2}) \times 2\pi e^2/h = \tfrac{1}{2} \times v_1$$

But $v_1 = 2 \cdot 188 \times 10^8$ cm/s (see Example 3·7)

$$\therefore \quad v_2 = 1/2 \times 2 \cdot 188 \times 10^8 \text{ cm/s} = 1 \cdot 094 \times 10^8 \text{ cm/s}$$

Example 3.9 Calculate the energy of an electron in the first Bohr orbit.

The energy of an electron in the nth Bohr orbit is given by

$$E_n = -2\pi^2 e^4 m/n^2 h^2$$

Since $n = 1$ for the first Bohr orbit,

$$E_1 = -2\pi^2 e^4 m/h^2 = -2 \cdot 180 \times 10^{-11} \text{ erg} = -13 \cdot 61 \text{ ev}$$

Example 3.10 Calculate the energy of an electron in the second Bohr orbit.

The energy of an electron in the second Bohr orbit is given by

$$E_2 = -\frac{2\pi^2 e^4 m}{(2)^2 h^2} = 1/(2)^2 \times -\frac{2\pi^2 e^4 m}{h^2} = 1/(2)^2 \times E_1$$

But $E_1 = -2 \cdot 180 \times 10^{-11}$ erg (see Example 3.9)

$$\therefore \quad E_2 = -0 \cdot 545 \times 10^{-11} \text{ erg} = -3 \cdot 402 \text{ ev}$$

It should be clear from the above discussion that the Bohr model provides a detailed and precise description of the motion of the electron in the hydrogen atom. Two pertinent questions can be asked at this stage, i.e. whether experimental evidence exists for quantisation, and how the experimental values compare with theory.

Franck and Hertz (1915) demonstrated that quantisation of energy (i.e. existence of energy levels) is a general feature present in all atoms and molecules. Their experimental arrangement is shown and explained in Fig. 3.27. Quantisation of angular momentum was also experimentally demonstrated soon thereafter. Thus, quantisation is a verifiable fact in the atomic and molecular domain.

The *ionisation energy* (IE) of the hydrogen atom (i.e. the energy needed to remove the single electron from the atom) can be measured either from the Franck-Hertz experiment or from the hydrogen atom spectra. IE is a positive quantity and its value is numerically equal to the ground state energy (E_1). This follows from the fact that if energy E_1 is supplied to the hydrogen atom in the ground state, the total energy of the electron in the atom will become zero. This means (see equation 3) that the electron, with zero velocity, is at infinite distance from the nucleus (i.e. the atom is ionised). Hence, E_1 is the ionisation energy and therefore, the magnitude of ionisation energy is equal to the ground state energy but opposite in sign. The experimental value of the ionisation energy of the hydrogen atom is 13·595 ev which agrees extremely well with the calculated value (see Example 3.9) of 13.61 ev.

It is possible to measure the *magnetic moment* of the hydrogen atom by observing its interaction with an externally applied magnetic field. However, the calculated and the measured values for the ground state do not agree at all thereby showing that the Bohr theory is not entirely correct. (We shall see later that the quantum mechanical theory is able to resolve this discrepancy.)

None of the other quantities like orbit radius, orbit velocity, etc., have been experimentally measured. Hence, Bohr's prediction about these cannot be verified. Although the exact radius of the hydrogen atom is not available, various experiments show that atomic radii are roughly
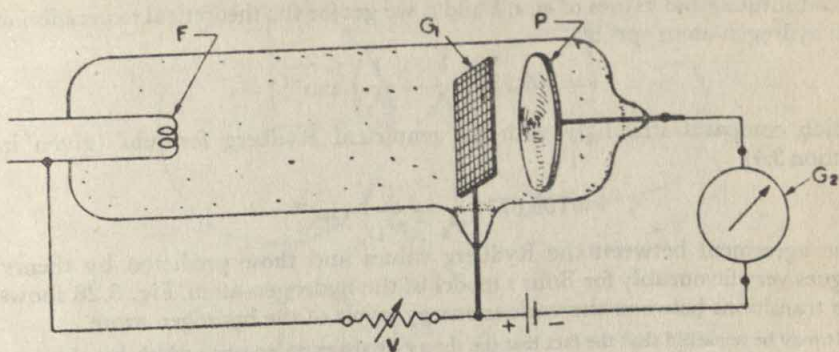
Fig. 3.27 The Frank-Hertz experiment to demonstrate quantisation of energy. Electrons released by the filament (F) are accelerated towards the grid (G_1) by the variable voltage V. The energy they acquire is proportional to V. A small but constant voltage is applied between G_1 and the plate P which collects the electrons. The current in the plate circuit is measured by the galvanometer G_2. The tube contains some gas at low pressure. The electrons from the filament collide with these atoms and molecules, but it is observed that unless the electrons have definite energies; that is, unless V has definite values (the values depending on the nature of the gas), no energy is lost to the atoms or molecules. (The energy loss is detected by the decrease in current in G_2.) The energy gained by the atoms or molecules is used to raise the electrons in these species to higher energy levels. This experiment thus shows that electrons in atoms and molecules can only accept definite and not arbitrary amount of energy.

of the order of an Angstrom. The calculated value of 0·529 A (see Example 3.5), conforms to this expectation.

Having discarded acceleration as the cause of radiation of electromagnetic waves, it was necessary to suggest an alternate mechanism to account for the origin of spectral lines. Bohr tackled this problem by introducing another *ad hoc* assumption namely that when the electron drops from a higher energy level to a lower energy level, the loss in electron energy shows up as radiation. He further postulated that the frequency, v, of the radiation and difference, ΔE, of the two energy levels are connected by the relation

$$\Delta E = hv$$

This is known as the *Bohr frequency rule*.* (Absorption of radiation is due to the reverse process of electron jump from a lower energy level to a higher energy level. The above equation is assumed to be valid for this case also.)

We shall now consider the special case of the hydrogen atom. Let E_{n_1} and E_{n_2} (where n_1 and n_2 are the principal quantum numbers such that $n_1 > n_2$) be the two energy levels between which the electron drops. From the energy expression and the frequency rule, it follows that

$$E_{n_1} - E_{n_2} = \Delta E = hv = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n^2_2} - \frac{1}{n^2_1}\right)$$

$$\text{or} \quad v = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{n^2_2} - \frac{1}{n^2_1}\right)$$

$$\text{or} \quad \bar{v} = \frac{2\pi^2 me^4}{h^3 c}\left(\frac{1}{n^2_2} - \frac{1}{n^2_1}\right)$$

*In proposing this rule, Bohr was guided by Einstein's photoelectric relation and Planck's solution of the black-body problem discussed earlier.

Substituting the values of m, e, h and c, we get for the theoretical expression of the hydrogen atom spectra,

$$\bar{\nu} = 109{,}737 \left(\frac{1}{n^2_2} - \frac{1}{n^2_1} \right) \text{ cm}^{-1}$$

which compares strikingly with the empirical Rydberg formula (given in section 3.4)

$$\bar{\nu} = 109{,}677 \left(\frac{1}{n^2_2} - \frac{1}{n^2_1} \right) \text{ cm}^{-1}$$

The agreement between the Rydberg values and those predicted by theory argues very favourably for Bohr's model of the hydrogen atom. Fig. 3.28 shows the transitions between the various energy levels of the hydrogen atom.

It may be remarked that the fact that the theory produces an equation which has the same form as the 'experimental' equation is no achievement. After all, the form of the theoretical equation is built into the two central assumptions namely the quantum condition and the frequency rule. What is truly remarkable about the theory is that the empirical Rydberg constant is calculated so precisely. Indeed, the agreement can be further improved by considering the motion of the nucleus which has been neglected in our simple treatment.

We now briefly state some of the refinements of the Bohr theory. Taking the clue from the solar system where the most general planetary orbit is an ellipse rather than a circle, Sommerfeld* (1915) introduced *elliptical orbits* for the electron in the hydrogen atom. Since in describing an ellipse, two radii (the
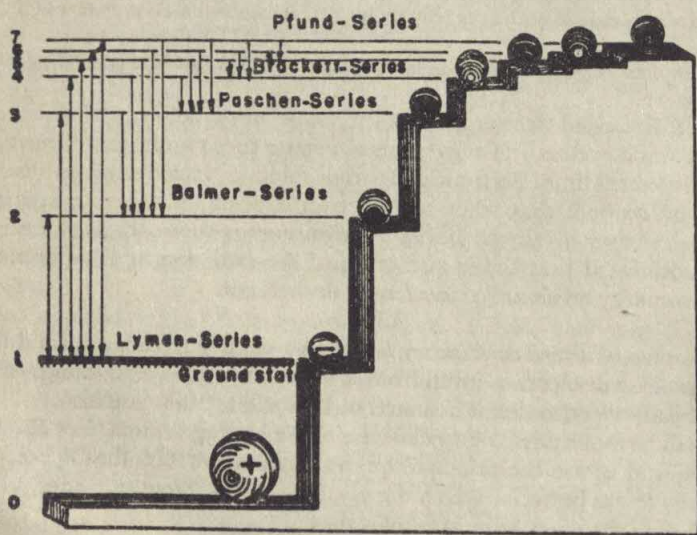
Fig. 3.28 The various energy levels of the electron in a hydrogen atom. No intermediate values are permitted. The situation is much the same as a ball on staircase. The ball can stay on any of the steps but not in between. Various transitions between the energy levels are shown giving rise to radiation. Each series is named after the discoverer who first observed them experimentally.

*Our treatment of Sommerfeld's ideas is not very precise. Our main interest here is to introduce those concepts which prove useful to understand the modern model of an atom.
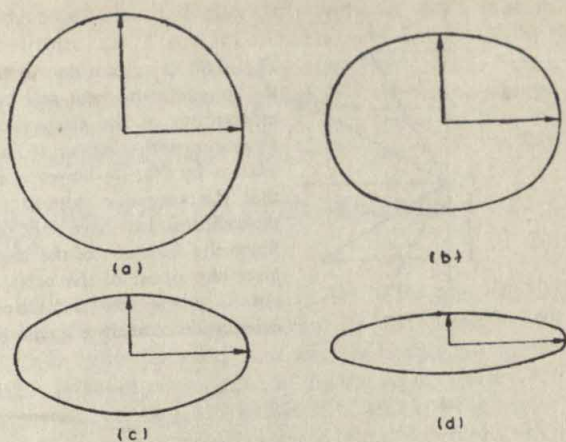
Fig. 3.29 In Bohr's theory only circular orbits were considered. The quantisation condition implied that circles of only certain radii were allowed. The quantum number needed for this purpose was related to the size of the orbit. When Sommerfeld extended the theory to elliptical orbits, the quantisation condition implied that both the semi-major and the semi-minor axes should have only certain values. In this figure are shown four possible choices of the semi-minor axes for a particular choice of the semi-major axis. The second quantum number needed for this purpose is connected with the shape of the orbit.

semi-major and the semi-minor) are required, the quantisation condition which restricts the (circular) radius in the Bohr model was extended to quantise the two radii separately. Inasmuch as the ratio of the radii measures the eccentricity (or shape) of an ellipse (Fig. 3.29), this step amounts to restricting the shapes of orbits. The second quantum number needed for this purpose was called the *azimuthal quantum number* (symbol l); l is related to the shape of the orbit.

The Bohr–Sommerfeld orbits, like the planetary ones, were planar. The electron magnetic moment is parallel to the angular momentum and both are perpendicular to the plane of the orbit. It was shown experimentally by Stern and Gerlach (1921) that this magnetic moment aligns itself in only certain directions with respect to the external magnetic field. This means that the direction of magnetic moment and hence the direction of angular momentum cannot have any arbitrary direction as in Fig. 3.30 (a), but only a few special directions (Fig. 3.30b). In other words, the electron orbit is limited to a few special planes. This feature was named as *space-quantisation*. It is convenient to indicate the direction of the orbit angular momentum by specifying its component along a reference direction. The quantisation of direction is equivalent to the quantisation of the components and the third quantum number was introduced to designate the permitted component. This was known as the *magnetic quantum number* (symbol m_l).

It was next found that many spectral and magnetic observations could not be explained on the basis of the orbit angular momentum and the associated orbit magnetic moment alone. Once again the planetary model suggested the
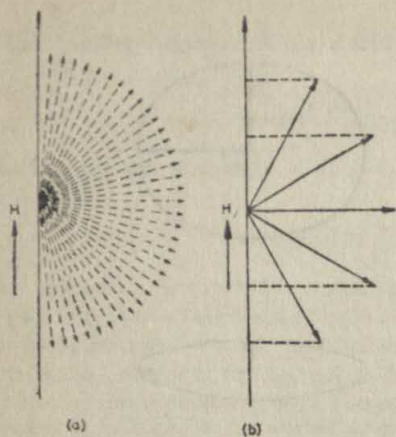
Fig. 3.30 (*a*) According to the classical laws, the magnetic moment and hence the angular momentum of the electron can point in any direction with respect to a magnetic field (shown by *H*); (*b*) however, experiments show that the magnetic moment (and the angular momentum) can have only certain directions. Since the direction of the angular momentum gives the plane of the orbit, this means that not only the size and shape, but also the orientation of orbits is quantised.

(a)   (b)

answer. Just as the planets spin around while moving in an orbit, it was assumed that an electron also spins about its axis during its orbit motion. This gives rise to spin angular momentum and spin magnetic moment. Experiments showed that spin angular momentum is also quantised with only two allowed orientations which were interpreted as corresponding to clockwise and anti-clockwise spinning motion (Fig. 3.31). The quantum number for this was called the *spin quantum number* (m_s).
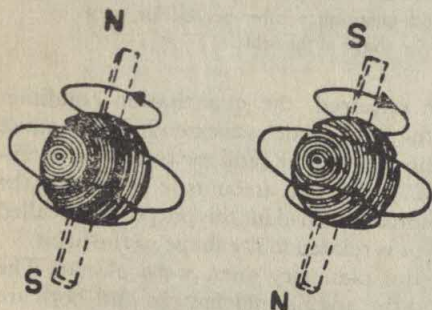
Fig. 3.31 The two possible spinning motions of an electron.

In short, the electron orbits in the Bohr-Sommerfeld model were characterised by four quantum numbers n, l, m_l, m_s. It will be seen in section 3.10.1 that these quantum numbers reappear in the modern theory. They cannot be, however, given as readily visualisable an interpretation as described above.

What can be said about the overall validity of the Bohr–Sommerfeld model? As is evident from our discussion, the theory was eminently successful in explaining the ionisation potential and the spectrum of the hydrogen atom. But a large part of its predictions (e.g. orbit radii, orbit velocities and so on) were unsupported by experiment.* The theory was logically unsatisfactory since it is a curious mixture of contradictory ideas. Further, its failure to account for the spectra of multi-electron atoms was an important limitation. An even greater

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*The quantum-mechanical model, it turns out, rejects precisely those parts of the Bohr model which were unverifiable.

drawback of the theory, from a chemist's point of view, was its inability to explain molecule formation. Thus, it cannot be said that the Bohr theory solved the atomic structure problem. Its primary contribution was that it pointed the path for further developments by highlighting the importance of quantum restrictions; its secondary contribution is that, even today, it provides an introduction to the subtleties of quantum behaviour.

3.8 DUAL NATURE OF MATTER—FAILURE OF CLASSICAL MECHANICS

Guided by the dual nature of radiation, Louis de Broglie, in 1923, conceived the idea that matter in general and electrons in particular, might also exhibit dual character. de Broglie deduced that the *wavelength*, λ, *of the electron wave* should be related to its momentum $p(=mv)$ by the equation $\lambda = h/p$. If electrons have wave character, they must exhibit diffraction—the most conspicuous property of waves. It was soon discovered that electrons do indeed show diffraction phenomena, thus establishing the dual nature of matter. The electron wavelength measured from diffraction patterns agreed exactly with the predicted value thus confirming the validity of the de Broglie relation. Fig. 3.32(a) shows a typical electron diffraction pattern which is strikingly similar to the pattern obtained from diffraction of the electromagnetic waves in the x-ray region, shown in Fig. 3.32 (b).

Fig. 3.32 The remarkable similarity between (a) electron diffraction, and (b) x-ray diffraction can be seen here. Since diffraction is a phenomenon which is incomprehensible on a particle model, one has to accept that electron has wave-like properties.
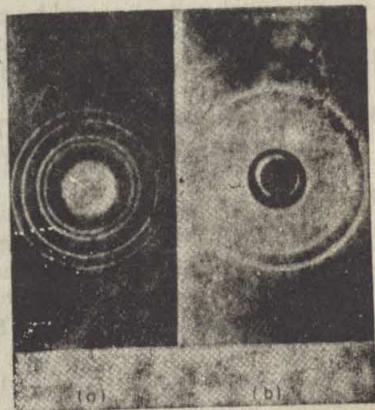
One may wonder that if matter has wave nature why could it not be detected prior to de Broglie's suggestion. The answer is readily provided by two sample calculations.

Example 3.11 Calculate the wavelength of a cricket ball (mass = 150 g) moving with a velocity of 200 cm/s.

The momentum (*mv*) of the cricket ball is 3×10^4 g cm/s. Therefore, from the de Broglie relation, the wavelength, λ, should be

$$\lambda = \frac{6 \cdot 63 \times 10^{-27}}{3 \cdot 00 \times 10^4} \approx 10^{-31} \text{ cm}$$

The diffraction effects for this wavelength can only be observed if the cricket ball encounters another object of similar dimension. Since objects of this size have not yet been discovered, the wave aspect of the cricket ball remains undetected.

Example 3.12 Calculate the wavelength of an electron (mass $=9\cdot1\times10^{-28}$ g) moving with a velocity of 10^8 cm/s. (We may recall that this is roughly the velocity in the first Bohr orbit in the hydrogen atom. This is also approximately the velocity an electron acquires when falling through a potential difference of 1000 volts as in an electron diffraction experiment.)

The momentum of the electron is $9\cdot1\times10^{-20}$ g-cm/s. Therefore $\lambda = \dfrac{6\cdot6\times10^{-27}}{9\cdot1\times10^{-20}} \approx 10^{-8}$ cm

This wavelength is of the order of atomic dimension and hence wave nature of electron can be detected in atomic and molecular domain. However, there are many situations as in Thomson's or Millikan's experiments where the electrons encounter only macroscopic obstruction (e.g. a glass tube or an oil drop, etc.) having sizes much larger than the electron wavelength. In these situations, it is entirely valid to discard the wave nature of the electrons as was (unintentionally!) done by Thomson and Millikan.

We have commented on several occasions in this chapter that Newtonian mechanics was found to be inadequate in describing electron behaviour. In the light of the calculations given above, it is now possible to pinpoint the reason for this failure. Classical mechanics treats matter as made up of ' pure ' particles ignoring the wave nature. Hence, the classical theory can be expected to work satisfactorily only in such situations where the wave aspect is insignificant. This usually is the case in macroscopic phenomena. In sub-atomic events, where the wave aspect is dominant, it is not surprising that the classical description proved erroneous. For the same reason a theory like Bohr's must be only partially correct since it too overlooked the wave character. The problem could only be solved by creating a new mechanics which does justice to the dual character. The new theory of quantum mechanics was evolved in the 1920's and it plays a central role in modern chemistry.

3.9 PRINCIPLES OF QUANTUM MECHANICS AND THE QUANTUM MECHANICAL MODEL OF THE HYDROGEN ATOM

The theory of quantum mechanics was independently and simultaneously formulated by Werner Heisenberg and Erwin Schrödinger during 1925–26. Important contributions to the theory were also made by Paul Dirac, Max Born and Wolfgang Pauli. Quantum mechanics gives a valid description for macro as well as micro matter. However, for macroscopic phenomena, its equations and its results become essentially identical to those of classical mechanics. Since the latter is mathematically simpler, it is preferred for the description of macroscopic phenomena. In the micro world, and in particular for phenomena connected with electrons, as in the atomic and molecular domain, quantum mechanics alone provides a satisfactory description.

3.9.1 The Uncertainty Principle

The conceptual viewpoint of quantum mechanics is built around the famous ' uncertainty principle '* first enunciated by Heisenberg in 1927. Heisenberg realised that the dual nature of matter and radiation imposes a serious limitation on the simultaneous determination of the position and the velocity of a body. To illustrate this, let us consider the problem of determining the position of an

*The uncertainty principle is contained in the Schrödinger equation—the basic equation of quantum mechanics—discussed in the next section. We, however, treat it first as it brings out very clearly the physical content of the theory.

electron. If we choose a radiation of wavelength λ to locate the electron, it can be shown that the electron cannot be located with an accuracy greater than $\pm\lambda$. In order to determine the position with a given precision, we have only to choose the appropriate wavelength. However, if we wish to determine the momentum of the electron simultaneously, the following difficulty arises. Because of the *de Broglie relation* $(\lambda=h/p)$ and the dual nature of radiation, the momentum of the incident photon increases as the wavelength of the radiation decreases. It is necessary that the photon and the electron collide so that the electron may be observed. The photon will disturb the momentum of the electron by an amount depending on the extent of the momentum transfer. It is obvious that the higher the momentum of the incident particle, the greater will be the disturbance, and hence the larger will be the uncertainty in measuring the momentum of the electron. Thus, as the precision in locating the electron increases, the precision in determining its momentum decreases. In other words, it is not possible to determine *simultaneously* the position and the momentum (or less accurately the velocity) of a body.

With the help of the de Broglie relation, we can translate this result into mathematical language. If the uncertainty in locating the position is $\pm\Delta x\,(=\pm\lambda)$, then the uncertainty in measuring momentum, Δp, will be roughly given by $\Delta p=h/\Delta x$. The product of these two uncertainties is, therefore,

$$\Delta p \times \Delta x = \Delta p \times (h/\Delta p) = h \tag{11}$$

Equation (11) is a statement of the uncertainty principle.

How serious are the implications of the uncertainty principle? We can answer this question by a calculation.

Example 3.13 If an electron is to be located within $0\cdot1$ A $(=1\times10^{-9}$ cm), what will be the approximate uncertainty in its velocity?

The approximate uncertainty in velocity (Δv) will be given by,

$$\Delta v = \frac{\Delta p}{m} = \frac{h}{m\Delta x} = \frac{10^{-27}}{10^{-27}\times10^{-9}} = 10^{9} \text{ cm/s}$$

This means that an attempt to locate the electron in the hydrogen atom with a precision of $0\cdot1$ A will lead to an uncertainty in its velocity of about 10^{9} cm/s. Since the electron velocity in the ground state according to the Bohr theory is 10^{8} cm/s we have the result that uncertainty in velocity is greater than the velocity itself! We can avoid this ridiculous statement by realising that when the electron position is specified reasonably accurately, it is meaningless to talk about its velocity at the same time.

The uncertainty principle forces a complete revision of the Newtonian idea of motion. According to the latter it is the function $x(t)$ which describes motion, but if $x(t)$ is known, it implies a simultaneous knowledge of the velocity.[*] Since this is impossible, we conclude that the function $x(t)$ is irrelevant and it is not possible to state the path of a body. Calculation of the trajectory of an electron in an atom or a molecule is, therefore, a futile exercise. We can now appreciate the major fault of the Bohr model. In calculating electron orbits precisely, Bohr was violating this fundamental requirement and hence his theory was only partially successful. We have remarked earlier that the orbit radii and orbit velocities have not been measured experimentally; uncertainty principle shows that it is impossible to measure these variables simultaneously.

Although our conclusion is strictly true in all cases, in macroscopic descriptions the Newtonian

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[*]This is so because from $x(t)$ we can calculate $(x_2-x_1)/(t_2-t_1)$, where x_2 and x_1 are the positions of the body at times t_1 and t_2 respectively. Velocity is the value of this ratio as t_2-t_1 becomes very small.

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scheme retains its utility since the uncertainties in position and velocity are small enough to be neglected as illustrated by the following example.

Example 3.14 If a cricket ball (mass = 150 g) is to be located within 0·1 A, what will be the approximate uncertainty in its velocity?

The approximate uncertainty (Δv) is

$$\Delta v = \frac{\Delta p}{m} = \frac{h}{m \Delta x} = \frac{10^{-27}}{150 \times 10^{-9}} \approx 10^{-21} \text{ cm/s}$$

Compared to the typical velocities of the ball, this uncertainty is negligible. Therefore, the uncertainty principle can be disregarded for macroscopic motion and one can then say that in such cases, the position and the velocity can be simultaneously determined to a reasonable precision.

Since the exact position and exact velocity cannot be simultaneously specified, quantum mechanics resorts to a probabilistic description.* For example, in an atom, it is possible to state the probabilities of the electron to be at various distances with respect to the nucleus. In the same way, probable values of velocity can also be given. It should be clearly understood, however, that a knowledge of probabilities for an electron to be at two locations carries no information as to how the electron 'moves' from one location to another. The quantum view of motion is indeed very strange compared to the classical view.

As far as other dynamical variables of an electron are concerned, we can show that the uncertainty principle leads to the following result. The total energy of an electron in an atom or molecule has a well-defined (sharp) value. The probability distributions as well as the sharp values can be calculated from a function designated as $\psi(x)$† and called the *wave function* or *the psi function*. $\psi(x)$ is obtained by solving the *Schrödinger equation* which is the fundamental equation in quantum mechanics in the same manner that Newton's equation is fundamental in classical mechanics.

3.9.2 The Meaning of Wave Function

The theory of quantum mechanics asserts that the wave function contains the maximum possible‡ description of motion of an object. In this sense the function $\psi(x)$ is the analog of the classical function $x(t)$. However, unlike $x(t)$ which denotes position (x) of the body at time t, $\psi(x)$ cannot be given a direct physical meaning.

For understanding atomic and molecular structure, we primarily need a knowledge of electron behaviour. This is given by the electronic wave functions obtainable by solving the Schrödinger equation for the appropriate atom or molecule. We have stated in the last section that only a few electron variables

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*Coin tossing provides a simple analogy. When a coin is tossed, it is not possible to state definitely whether 'heads' or 'tails' will show up. However, we are certain that heads (or tails) will come with 50 per cent probability.

†This is true for one-dimensional motion. In three-dimensions the form of the function is $\psi(x, y, z)$. The most general form contains the time variable also but the time-dependence is not relevant for most of atomic and molecular discussion.

‡The term 'maximum possible' has been used because 'complete' description in the classical sense is inadmissible because of the uncertainty principle.

(e.g. energy) have sharply defined values in atoms and molecules. It is possible to obtain these values, once the wave function is known. Calculations show that the energy and angular momentum in atoms (and the energy in molecules) are quantised. It is a particularly pleasing feature of the quantum approach that quantisation, which is experimentally verifiable but which was introduced *ad hoc* in the Bohr model, emerges automatically from the Schrödinger equation. For the variables which do not have sharp values, probability distributions can be calculated from $\psi(x)$. The probability distribution for position is represented by the square of the wave function $\psi^2(x)$ and this is important for a qualitative understanding of atomic and molecular structure as will be presently seen.

The quantum description is rather subtle and difficult to get accustomed to because it seems contrary to our familiar experience.* One may wonder why such a radical and strange viewpoint is accepted. The reason is because its consequences are in complete accord with experiment. This, after all, is the only yardstick a scientific theory is judged by. The significance of quantum mechanics to chemistry is that it provides a unified treatment of atomic and molecular structure. Thus, electron behaviour as described by a wave function accounts for the electronic structure of atoms, the periodicity of atomic properties, the formation of molecules and the nature of the chemical bond, the shapes and geometry of molecules and the correlation of microscopic structure with macroscopic behaviour. However, we emphasise that the understanding of chemical phenomena through quantum mechanics is only qualitative at present. This is due to mathematical difficulties which prevent the exact solution of Schrödinger's equation for all chemical systems except hydrogen atom and hydrogen molecule ion. The hydrogen atom as well as the hydrogen molecule ion are one-electron systems and exact wave functions for them can be obtained from Schrodinger's equation. In these two cases, properties can be calculated quantitatively and they are found to be in perfect agreement with experiment. For all other atomic and molecular systems, exact wave functions are not available and we have to resort to approximations which make the quantum approach qualitative or at best semi-quantitative.

3.10 QUANTUM MECHANICAL MODEL OF THE HYDROGEN ATOM

In this section we shall construct the quantum mechanical model of the hydrogen atom. For this, we first state some general conclusions that emerge from the exact mathematical treatment. We shall then use the graphical and pictorial language to depict the electron behaviour.

3.10.1 Some General Conclusions

(*i*) There are infinite number of wave functions for the electron in the hydrogen atom. This feature is alternatively expressed by the statement that there is an infinite number of orbitals for the electron in the hydrogen atom. The term '*atomic orbital*' is used for an electron wave function since the wave function gives the maximum possible information about electron motion in an atom. The term 'orbital' is reminiscent of orbits of the Bohr theory, *but it must be remembered that orbitals do not define a definite path for the electron; rather, they define only the probabilities of the electron being in various regions of space around the*

*** Because atomic behaviour is so unlike ordinary experience, it is very difficult to get used to and it appears peculiar and mysterious to everyone, both to the novice and to the experienced scientist. Even the experts do not understand it the way they would like to, and it is perfectly reasonable that they should not, because all of direct, human experience and of human intuition applies to large objects. We know how large objects will act, but things on a small scale just do not act that way. So we have to learn about them in a sort of abstract or imaginative fashion and not by connection with our direct experience ', from *Feynman Lectures on Physcis* Vol. I, Chapter 37.

nucleus. Also, orbits are necessarily planar (i.e. two-dimensional) but orbitals give a three-dimensional distribution.

(ii) In each orbital, the electron has precise energy. The magnitudes of the angular momentum, as well as one component of the angular momentum, in a reference direction are also sharp. The other two components of the angular momentum do not have fixed values. In other words, the direction of the electron angular momentum is only partially specified.*

(iii) The values of the energy, the angular momentum, as well as of the component of the angular momentum change discontinuously from one orbital to another (i.e. the energy and the angular momentum of the electron in the hydrogen atom are quantised). These features, first encountered in the Bohr theory, are supported by experiment. The major difference is that the magnitude and component of angular momentum in the Bohr model were related to a precise orbit and a precise orientation of the orbit, while such an interpretation is not permissible in the Schrödinger model.

(iv) All other dynamical variables like position, velocity, etc., do not have sharply defined values. For these variables, only probability distribution functions exist and these can be obtained from the wave function. The square of the wave function, ψ^2, directly gives the position probability distribution for a particular orbital. ψ^2 varies from place to place and its value at a particular point measures the probability of finding the electron at that point. In what follows, only position probability distribution is needed.

(v) The permitted values, E_n, of energy (energy levels) are given by the formula $E_n = -2\pi^2 me^4/n^2 h^2$, which is identical to that obtained by the Bohr theory. As before, n is called the *principal quantum number* with only non-zero positive integral values 1, 2, 3 to ∞.

(vi) For a given value of the energy, the angular momentum cannot have any magnitude. The permitted values of the magnitude of angular momentum, L, for an energy level with quantum number n are given by the formula,

$$L = \sqrt{l(l+1)}\ (h/2\pi)$$

where l can have any positive integral value from zero to $n-1$; l is known as the *azimuthal quantum number*.

Example 3.15 What are the permissible values of l for $n=3$?

The minimum value of l is always zero and the maximum value is always $n-1$. In this case $n=3$, so the maximum value of l is 2. The permitted values, therefore, are 0, 1 and 2.

Example 3.16 Calculate the magnitude of the orbital angular momentum for $l=1$ and $l=3$.

The magnitude of the orbital angular momentum is given by

$$L = \frac{h}{2\pi}\ \sqrt{l(l+1)}$$

$$\text{For } l=1,\ \sqrt{l(l+1)} = \sqrt{2}$$

$$\therefore L = \sqrt{2} \times 1\cdot0545 \times 10^{-27} \text{ erg.s}$$
$$= 1\cdot49 \times 10^{-27} \text{ erg.s}$$

$$\text{For } l=3,\ \sqrt{l(l+1)} = \sqrt{12}$$

$$\therefore L = \sqrt{12} \times 1\cdot0545 \times 10^{-27} \text{ erg.s}$$
$$= 3\cdot651 \times 10^{-27} \text{ erg.s}$$

*It can be shown that simultaneous specification of direction and magnitude violates the uncertainty principle.

Fig. 3.33 The meaning of m_l quantum number. An angular momentum vector with quantum number l (i.e. with magnitude $\sqrt{l(l+1)}$) can point in only such directions with respect to an external magnetic field that its components along the field direction have integer values ranging from $-l$ to $+l$ in units of $h/2\pi$. This figure shows the three permitted directions for the value $l=1$ with component m_l having values $+1$, 0 and -1.
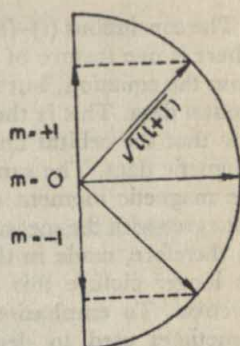
(*vii*) For a particular value of the magnitude of angular momentum, there can be only certain components in a reference direction (see Fig. 3·33). These components have values m_l $(h/2\pi)$, where m_l is an integer with any of the values from $-l$ to $+l$. m_l is known as the *magnetic quantum number*. l and m_l together are called the *angular momentum quantum numbers*.

Example 3.17 What are the permissible values of m_l for $l=3$?

The permissible values of m_l range from $-l$ to $+l$ in steps of one. Hence for $l=3$ they are -3, $-2, -1, 0, +1, +2, +3$. In general there are always $(2l+1)$ values of m_l for a given value of l.

(*viii*) The magnitude of magnetic moment (μ_L) is again given by equation (10) derived earlier in the Bohr theory. In view of (*vi*), the equation becomes.

$$\mu_L = \frac{eh}{4\pi mc} \sqrt{l(l+1)}$$

Example 3.18 Calculate the orbital magnetic moment for states $l=1$ and $l=3$.

The magnitude of the orbital magnetic moment is given by

$$\mu_L = \frac{eh}{4\pi mc} \times \sqrt{l(l+1)}$$

On substituting values of e, h, π, m and c

$eh/4\pi mc$ $= 9{\cdot}2732 \times 10^{-21}$ erg/gauss

For state of $l=1$, $\mu_L = \sqrt{2} \times 9{\cdot}2732 \times 10^{-21}$ erg/gauss
$= 13{\cdot}11 \times 10^{-21}$ erg/gauss

For state $l=3$, $\mu_L = \sqrt{12} \times 9{\cdot}2732 \times 10^{-21}$ erg/gauss
$= 32{\cdot}12 \times 10^{-21}$ erg/gauss

Every permitted combination of the three quantum numbers n, l, m_l defines a permitted orbital. For convenience, atomic orbitals are designated by symbols. Orbitals with $l=0$, $l=1$, $l=2$, $l=3$ are called as s, p, d and f orbitals respectively. Higher angular momentum values are labelled thereafter in alphabetical sequence (e.g. $l=4$, g orbital; $l=5$, h orbital). The principal quantum number of the orbital is given before the angular momentum symbols. Thus, the ground state orbital of hydrogen atom is written as $1s$. The m_l quantum number is indicated by appropriate numerical subscripts (e.g. p_{+1}, d_{-2} etc.) or by alphabetical subscripts (e.g. p_x, d_{xy}, etc.).*

*The significance of designations like p_x, d_{xy}, etc., will be discussed later.

The conclusions (*i*)–(*viii*) given above follow from the Schrödinger equation. There is one feature of the hydrogen atom which, however, does not emerge from the equation, but is introduced in an *ad hoc* manner to interpret experimental data. This is the concept of the electron spin. In the Bohr theory we saw that the orbital angular momentum alone was not sufficient to explain magnetic data. The same situation prevails in the Schrödinger theory where the magnetic moment calculated from the orbital angular momentum does not agree with the measured value. The assumption of spin angular momentum is, therefore, made in the Schrödinger model also.* It turns out that one can no longer picture this additional angular momentum as due to a spinning electron. To emphasise this fact, the term intrinsic angular momentum is sometimes used to denote spin angular momentum. Fig. 3.34 shows the
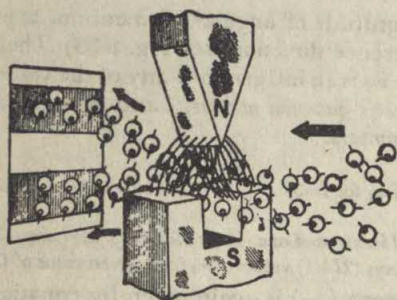
Fig. 3.34 If hydrogen atoms (in the ground state) are passed through an inhomogeneous magnetic field, the beam is split into two parts. This interaction with the magnetic field shows that the atoms must have magnetic moment. However, the moment cannot be due to the orbital angular momentum since *l*=0. Hence one must assume existence of intrinsic angular momentum, which, as the experiment shows, has only two permitted orientations.

experimental arrangement which demonstrates the existence of intrinsic angular momentum. The magnitude of the spin angular momentum, *S*, is given by

$$S = \sqrt{s(s+1)}\, h/2\pi \quad \text{where } s = 1/2$$

There are only two allowed components of the spin angular momentum along a reference direction given by $1/2(h/2\pi)$ and $-1/2(h/2\pi)$ (Fig. 3.34). The quantum number which designates this is called the *spin quantum number, m_s*. It has the value $+1/2$ or $-1/2$. The spin quantum number is indicated where necessary by arrows ↑ or ↓ symbolising up or down spin orientation respectively. The spin magnetic moment μ_s is given by the expression

$$\mu_s = \frac{eh}{2\pi mc} \sqrt{s(s+1)}$$

To sum up then, *the electron behaviour in the hydrogen atom is characterised by four quantum numbers n, l, m and m_s*. Their possible combinations are summarised in Table 3.3

3.10.2 Graphical Representation of the Hydrogen Atom Orbitals

The similarities and the differences in electron behaviour in different orbitals are easily comprehended from the graphical plots of the wave function ψ and of the probability function ψ^2, both of which vary with the position of the electron. The electron position with respect to the nucleus is most conveniently

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*It is not necessary to make this assumption in the relativistic version of the Schrödinger theory, first given by Dirac (1928). Electron spin emerges as a consequence of the Dirac equation.
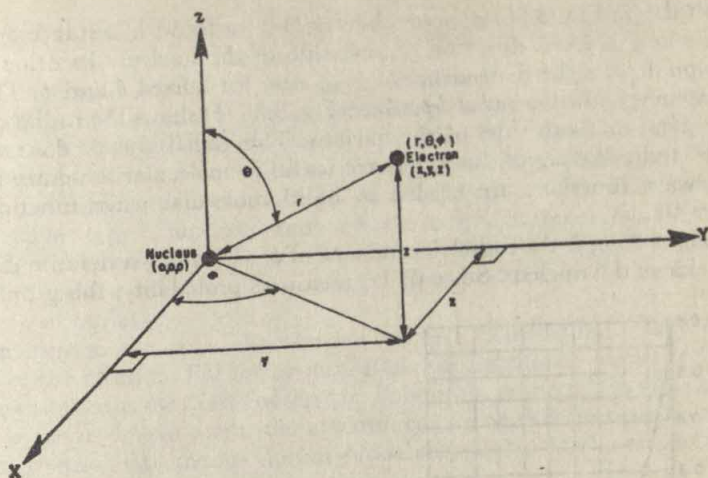
Fig. 3.35 The position of an electron with respect to the nucleus as the origin (0, 0, 0) is most usually specified in atomic structure discussions by r, θ and ϕ. The meaning of these three coordinates is shown in the figure. Also shown in the figure are the cartesian coordinates (x, y, z) for sake of comparison.

specified by the three spherical polar coordinates r, θ and ϕ (Fig. 3.35). ψ and ψ^2 are now functions of the three variables r, θ and ϕ. The simultaneous dependence of a quantity on three variables cannot be shown on paper (or even in three-dimensions, for that matter). Therefore, several less complete ways have been devised for the purpose. Different plots bring out different features of electron behaviour as we shall now show by discussing a few specific orbitals. The student should carefully study all of these since they collectively provide the much needed visualisation of electron motion.

Table 3.3 Possible Combinations of Four Quantum Numbers

n	l (values range from 0 to $n-1$)	m_l (values range from $+l$ to $-l$)	m_s	Number of combinations	Designation
1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$1s$
2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$2s$
	1	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6	$2p$
3	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$3s$
	1	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6	$3p$
	2	$+2, +1, 0, -1, -2$	$+\frac{1}{2}, -\frac{1}{2}$	10	$3d$
4	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$4s$
	1	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6	$4p$
	2	$+2, +1, 0, -1, -2$	$+\frac{1}{2}, -\frac{1}{2}$	10	$4d$
	3	$+3, +2, +1, 0, -1, -2, -3$	$+\frac{1}{2}, -\frac{1}{2}$	14	$4f$

1s orbital: (*i*) Fig. 3.36 (*a*) shows how ψ (1s) varies with distance from the nucleus along a fixed direction on one side of the nucleus. In other words, this graph depicts the dependence of $\psi(1s)$ on r for a fixed θ and ϕ. This type of variation is known as *radial dependence*. Fig. 3.36 (*b*) shows the radial dependence of $\psi(1s)$ on both sides of the nucleus. The radial ψ plots do not have any direct physical significance, but are useful in molecular structure because atomic wave functions are needed to build molecular wave functions (see Chapter 4).

(*ii*) Fig. 3.36(*c*) is the radial dependence of ψ^2 (1s) along a definite direction on one side of the nucleus. Since $\psi^2(1s)$ measures probability, this graph shows

(a)

(b)

(c)

(d)
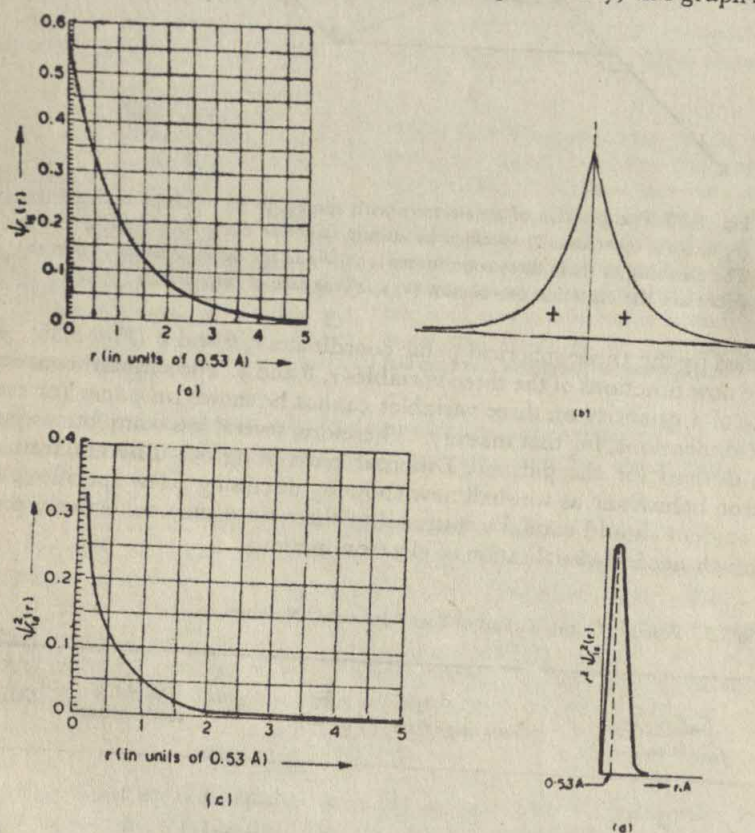
Fig. 3.36 (*a*) The dependence of the 1s wave function (ψ1s) plotted as a function of distance (*r*) from the nucleus in a particular direction on one side of the nucleus only. (*b*) The dependence of ψ1s or r on both sides of the nucleus in a particular direction. The positive sign [not shown in (*a*)] indicates that ψ1s is positive everywhere. This graph will be useful in molecular structure discussions (Chapter 4). (*c*) The probability of finding the electron as a function of r in a particular direction. Note that the probability never strictly becomes zero no matter how large the distance is, but it does become very small beyond 1.5 A. (*d*) The radial distribution function for the electron in the ground state. The maximum occurs at 0.53 A which is called the most probable distance of the electron in the 1s state. The probability values in this graph are the probabilities for a particular distance, integrated (i.e. added together) over all possible directions.

that the probability of finding the electron decreases rapidly as the distance from the nucleus increases. The feature to note here is that though probability becomes very small beyond 1.5 A, it never becomes exactly zero.

(*iii*) In Fig. 3.36(*c*), each point on the curve gives the probability at a particular distance for a definite direction. Sometime, it is more useful to know the total probability at a particular distance *irrespective of direction*. This is obtained by adding the probabilities in all directions for that particular distance. This type of function, known as the *radial distribution function*, for the 1*s* orbital is shown in Fig. 3.36(*d*). Mathematically, Fig. 3.36(*d*) is obtained by multiplying the ordinate of Fig. 3.36(*c*) by $4\pi r^2$ which is the surface area of a sphere of radius *r*.

The maximum in a radial distribution function indicates the most probable location of the electron. For the ground state, the maximum occurs at 0·53 A, the same distance as the radius of the first Bohr orbit. Although in the quantum picture of the hydrogen atom, the electron can be at different distances with different probabilities, the maximum probability is still at the same distance as in the Bohr model.

Radial distribution functions are most useful in energy considerations since electron-nucleus potential energy (e^2/r) depends on distance only and is independent of direction. Radial distribution functions therefore help us to understand the relative energies of orbitals in multi-electron atoms (section 3.11.1).

(*iv*) Let us now consider the dependence of ψ_{1s} on θ and ϕ for a fixed distance. This type of variation, known as angular dependence, is three-dimensional since there are two independent angular variables. It so happens that all *s* orbitals have no angular dependence, i.e. ψ_{ns} for all *n* has the same value for a particular distance in any direction. In other words, all *s* orbitals are spherically symmetrical. The shape of ψ_{1s} as a function of angles (for fixed distance) is shown in Fig. 3.37 [(*a*) is the 'photographic' view and (*b*) is the cross-sectional view]. The angular ψ-plots, like the radial ψ-plots, have no direct physical significance, but they are important for understanding molecular shapes (see Chapter 4).

Fig. 3.37 (*a*) The 'photographic' view of the angular dependence of ψ_{1s} for a fixed distance. In three-dimensions this would be a sphere. 1*s* orbital is, therefore, called spherically symmetrical. (*b*) The cross-section view of ψ_{1s}.

(*a*)   (*b*)
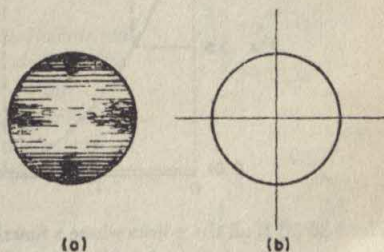
(*v*) For *s* orbitals, since ψ is independent of angles, the probability (i.e. ψ^2) is also independent of angles, i.e. the probability is also spherically symmetric. Consequently, Fig. 3.37 represents the angular variation of the probability for the 1*s* orbital* equally well.

(*vi*) The simultaneous dependence on distance and angles of ψ_{1s} and ψ^2_{1s} can be visualised by mentally combining the appropriate parts of Figs.

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*This is not true in general. For *p*, *d*, *f* and other non-zero angular momentum orbitals, the angular variation of ψ^2 differs from the angular variation of ψ—as shown in Fig. 3.41

3.36 and 3.37. However, partial pictorial representation of the simultaneous dependence can be obtained in several ways which are sometimes quite useful. We now illustrate one of the ways with reference to the $1s$ orbital. If we plot probability values for the ground state as a function of r, θ, ϕ and join all the points having equal values, we will get a diagram—called contour diagram—consisting of a series of concentric spheres with the nucleus at the centre. The cross-section of such a diagram will obviously be a series of concentric circles. Fig. 3.38 shows the cross-section of three of the infinite number of probability contours. In Fig. 3.38(a), the numbers on each circle give the value of the (constant) probability for a distance equal to the radius of the circle. As re-marked earlier, the probability falls off rapidly with distance. In Fig. 3.38(b),
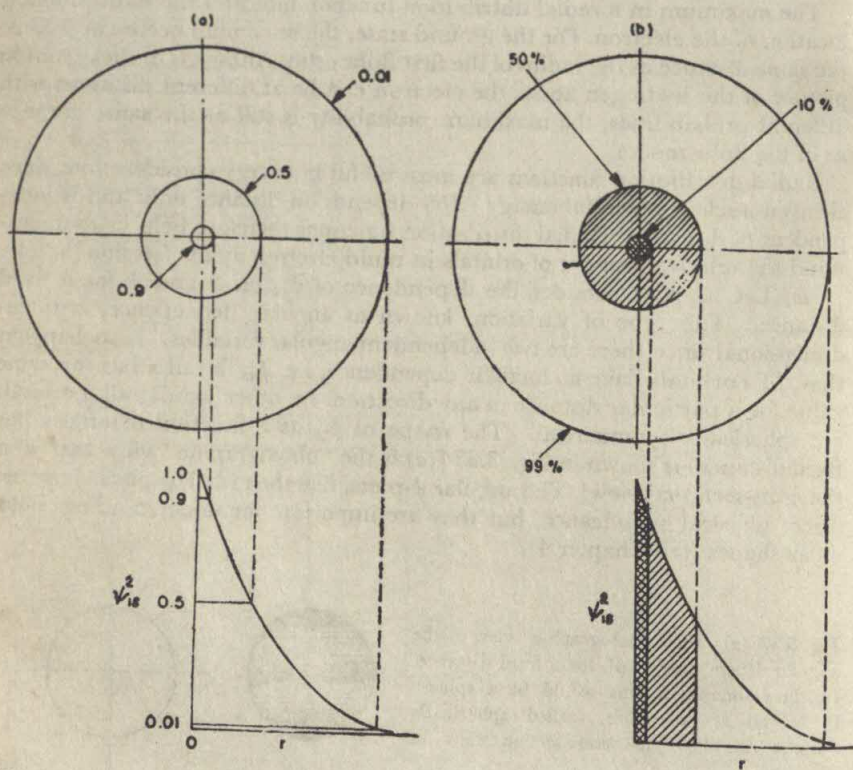
Fig. 3.38 (a) If all the points where a function has the same value are joined, one gets what are known as contours of the function. Since the $1s$ orbital is spherically symmetric, the probability of finding an electron at a particular distance is the same in all directions. Hence the proba-bility contours of the $1s$ orbital will be a series of concentric spheres in three dimensions and a series of concentric circles in two dimensions. The latter are shown in the above figure. The numbers on each circle denote the probability value at a distance corresponding to the radius of the circle. Note that contour diagrams contain radial as well as angular dependence.

(b) It is more informative to know how much probability is enclosed by each of the contour spheres. This is shown in this figure for the circles corresponding to the spheres. As the radius becomes larger, greater probability is enclosed within but only a circle of infinite radius can contain the entire probability, i.e. can contain the electron. The outermost circle in this figure encloses 99 per cent probability.

the number on each circle gives the probability percentage of the electron to be found within the volume enclosed by the corresponding sphere in three-dimensions. For example, the outermost circle encloses 99 per cent probability; there being only one per cent chance of finding the electron outside. Since the radial probability becomes zero only at infinite distance from the nucleus (Fig. 3.36c), it follows that only a sphere with infinite radius can ' completely contain ' the electron. But since this cannot be drawn, we can say, as a fair approximation, that the sphere corresponding to the outermost circle in Fig. 3.38, *almost* defines the boundary of electron motion in the ground state of the hydrogen atom. We hope, however, that the student appreciates the fact that the notion of boundary surfaces and of atomic sizes has only approximate validity in the quantum model.*

(*vii*) Perhaps the most visual representation of the simultaneous dependence is shown in Fig. 3.39(*a*), which has been obtained by using dots in such a way that the density of dots is proportional to the probability value. One interpretation of this figure is that the dots represent a number of probable instantaneous positions of the electron. Another interpretation is to imagine that a series of photographs of a vast number of hydrogen atoms has been merged into a single photograph.

(a)

(b)

(c)

Fig. 3.39 (*a*) In this figure dots are marked in such a manner that the density of dots is proportional to the probability. Again, we are showing here only a two-dimensional view. If a long-duration exposure photograph of a hydrogen atom could be taken the picture would be like this figure. On the other hand, if instantaneous pictures of a very large number of hydrogen atoms could be fused into a single picture, it would also look like this figure.

(*b*) The circle here is the cross-section of the three-dimensional sphere which encloses 99 per cent of the dots. The circle has the same significance as the outermost circle in Fig. 3.38 (*b*).

(*c*) We have removed the dots from (*b*) for simplicity and retained the circle only. The three-dimensional sphere corresponding to this is sometimes called as the boundary surface.
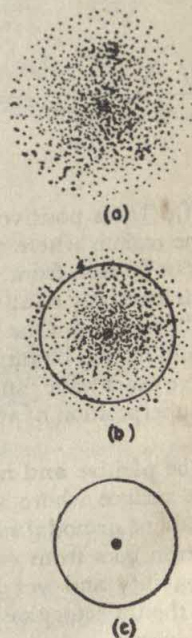
If we draw a sphere which encloses 99 per cent of the dots, the cross-section view would look as in Fig. 3.39(*b*). For simplicity, one can dispense with the dots and only draw the circle (Fig. 3.39c). This circle would have the same

*The choice of ' 99 per cent ' is, of course, arbitrary. Any other number like 95 per cent or 99·9 per cent could have been chosen with equal justification. This reemphasises the point that boundary or size of an atom does not have absolute significance.

significance as the circle in Fig. 3.38(*b*).* This is the simplest representation of the 1*s* orbital but it can be misleading if not properly understood.

Higher energy orbitals: The representations of orbitals with higher values of *n* and *l* become increasingly complicated. They are shown in Figs. 3.40 to 3.45. The various plots are interpreted in exactly the same way as the plots for the 1*s* orbital. A few additional features, not present in the 1*s* orbital, are described in the following.
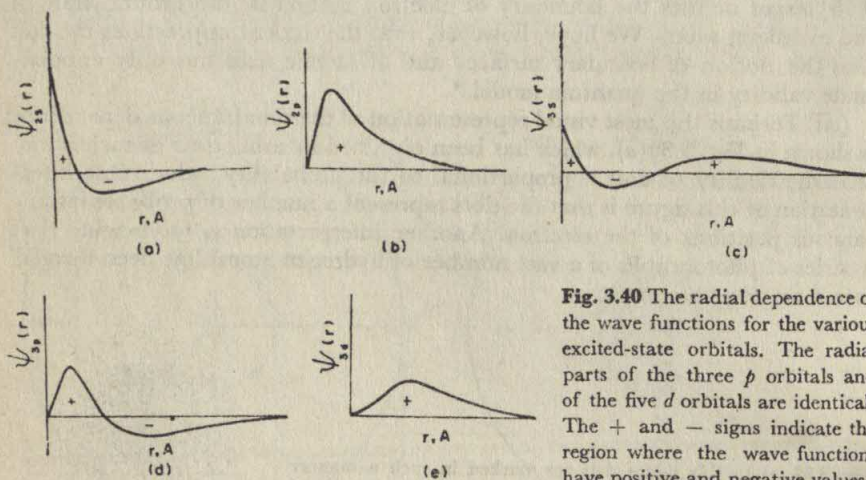
Fig. 3.40 The radial dependence of the wave functions for the various excited-state orbitals. The radial parts of the three *p* orbitals and of the five *d* orbitals are identical. The + and − signs indicate the region where the wave functions have positive and negative values.

(*i*)ψ(1*s*) is positive everywhere, but wave functions of other orbitals have some regions where they are positive and some others were they are negative as can be seen from the radial and angular plots in Figs. 3.40 and 3.41. The signs have only relative significance. ψ^2 is, of course, always positive irrespective of the sign of ψ. One may ask, if ψ does not have direct physical meaning, why should its sign be important? The answer to this is that in molecular systems, where exact wave functions are not available, approximate ones are constructed by superposition of atomic orbitals. In superposition, relative signs play crucial role.

The positive and negative regions are separated either by a point or a line or a surface where the probability is zero. These are called nodal point, nodal line or nodal surface respectively. If the student is puzzled as to how an electron goes from one place of finite probability to another place of finite probability and yet have zero probability in between, he must remember that the trajectory or path of an electron has no meaning within the quantum framework.

(*ii*) All orbitals with $l \neq 0$ have angular dependence. Therefore, *p* and *d* and other higher angular momentum orbitals are not spherically symmetrical (Fig. 3.41). The angular dependence of the three *p*-orbitals is such that they

*The circle in Fig. 3.37(*b*), however, should not be confused with those in Figs. 3.38(*b*) and 3.39(*c*). The former is a cross-section of only the angular (θ, ϕ) variation while the latter are cross-sections of the total (r; θ, ϕ) dependence. Only for the 1*s* orbital, the two dependences happen to have similar form.
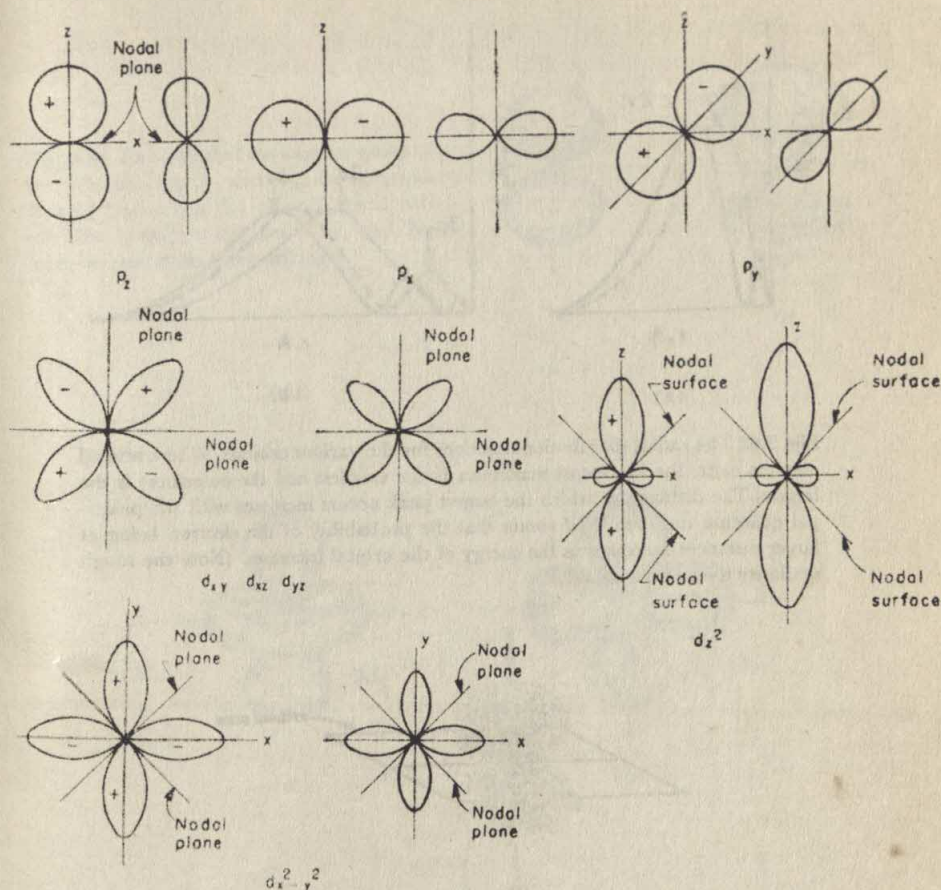
Fig. 3.41 The angular dependence of the wave functions and of the probability functions for the various orbitals. The angular parts of $2p$, $3p$, $4p$, etc. or $3d$, $4d$, $5d$, etc., are identical. Only cross-sections are shown here. The signs in the wave function graphs have only relative significance. Signs have not been indicated in the probability graphs since they are necessarily positive everywhere. Note the directional character of the p and d orbitals which is important for understanding the shapes of molecules.

have the same shape, but are oriented along the three mutually perpendicular directions. The orbitals are named as p_x, p_y and p_z orbitals.

(*iii*) The radial distribution function of the $2s$ orbital (Fig. 3.42a) shows two maxima, a smaller one near the nucleus and a bigger one at a larger distance. Comparing the location of the maximum in the $2s$ orbital with the maximum in the $1s$ orbital, we conclude that an electron in the $2s$ orbital has greater probability to stay further away than an electron in the $1s$ orbital.

(*iv*) The radial distribution function of the three $2p$-orbitals is identical. It shows only one maximum which is at a greater distance than the $1s$ maximum. This means that a $2p$ electron is further away from a $1s$ electron and has a much smaller probability compared to a $2s$ electron to be found near the
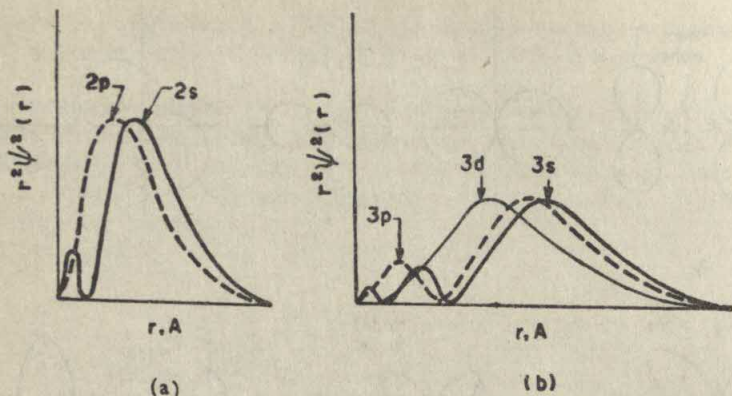
Fig. 3.42 The radial distribution functions for the various orbitals. Where several maxima exist, the innermost maximum is the smallest and the outermost is the largest. The distance at which the largest peak occurs increases with the principal quantum number. This means that the probability of the electron being at larger distances increases as the energy of the orbital increases. (Note the rough similarity to the Bohr model.)
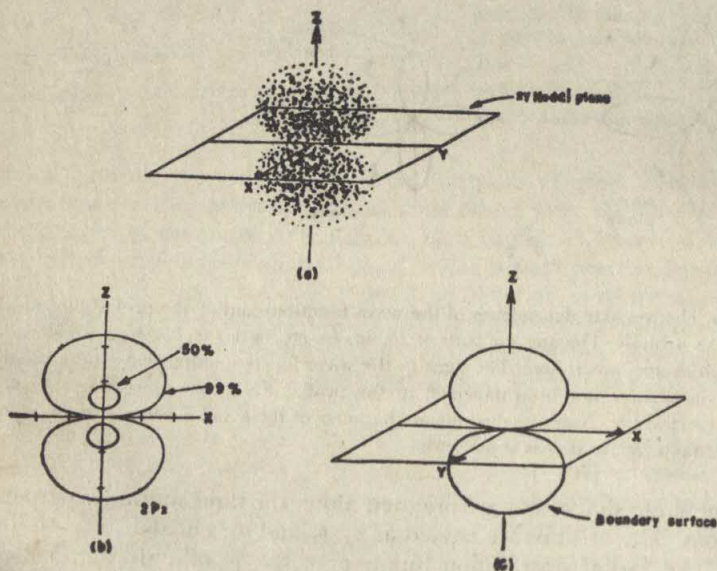
Fig. 3.43 The electron dot, the contour and the boundary surface representation of the $2p_z$ orbital. The $2p_x$ and the $2p_y$ orbitals are obtained by aligning these figures along the x- and y-axes respectively.

nucleus. For this reason we say that a $2s$ orbital penetrates closer to the nucleus than a $2p$ orbital. In general, higher the angular momentum, lesser is the penetration close to nucleus, as shown in Fig. 3.42.

The group of orbitals with the same value of n is said to define a shell, $n=1$ is called the K shell, $n=2$, the L shell and so on. Sometimes orbitals having

Fig. 3.44 The fact that the angular parts of two orbitals (say $2p_z$ and $3p_z$) are identical does not mean that the orbitals are identical. The boundary surfaces of $2p_z$ and $3p_z$ bring out the differences strikingly.

$2p_z$

$3p_z$

(a)

(b)

$3d_{z^2}$

$3d_{x^2-y^2}$

(a)

(b)

$3d_{xy}$

$3d_{xz}$

$3d_{yz}$

(c)

(d)

(e)
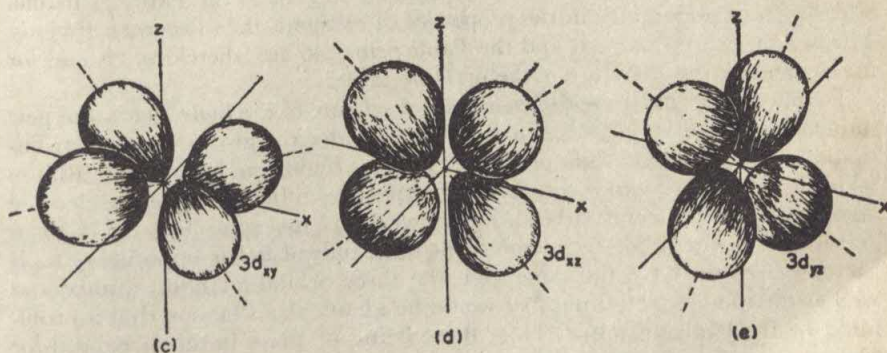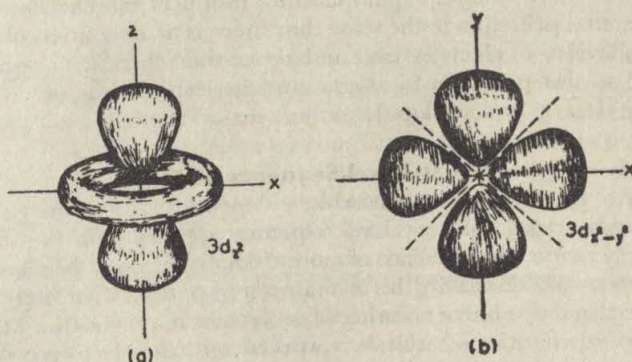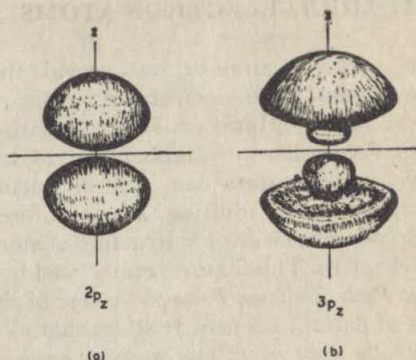
Fig. 3.45 The boundary surfaces of the five $3d$ orbitals

the same value of l within a shell are said to define a sub-shell.

Had the charge of an electron been smeared out in space, instead of being localised at a point, then ψ^2 would simply be a measure of the charge density. The ψ^2 graphs in that case would represent the electron charge cloud in various orbitals. Although there is conclusive evidence that an electron is not smeared out, suggesting that this interpretation is not correct, the charge cloud model is often used to simplify an argument.

3.11 MULTI-ELECTRON ATOMS

The hydrogen atom orbitals provide the basis for the treatment of multi-electron atoms. Each electron, in a many-electron atom, is considered as moving in an atomic orbital which is qualitatively similar to the hydrogen atom orbitals. Four quantum numbers are needed to specify each of the orbitals, as in the hydrogen atom case, and the quantum numbers have the same physical significance. In addition, a new feature is needed to understand the relationship between electronic structure of atoms and the physico-chemical behaviour of elements. This feature, enunciated by Wolfgang Pauli in 1925 and known as the *Pauli Exclusion Principle*, is one of the most far-reaching generalisations in all of natural science. It states that *no two electrons in an atom (or molecule) can have the same set of four quantum numbers.* In other words, an atomic orbital (quantum numbers n, l, m_l) can accommodate a maximum of two electrons if the electrons have different spin quantum numbers m_s. The Pauli principle is a fundamental principle in the sense that there is no derivation of it. It regulates the behaviour of electrons over and above the Schrodinger equation. The importance of this principle in atomic and molecular structure will become abundantly clear as we develop the subject further.

3.11.1 Deriving the Energy Level Sequence of Orbitals

The energy of the hydrogen atom orbitals depends on the principal quantum number n only and the energy level sequence appears as in Fig. 3.46(*a*). In the rest of the atoms, the presence of more than one electron brings in electron repulsion effects which modify this orbital energy pattern. Our first task, therefore, is to obtain the relative ordering of orbitals in multi-electron atoms. Once the sequence of energies of orbitals is worked out, the electronic structure of atoms of various elements is obtained simply by putting in one electron at a time in the lowest energy orbital available, subject to the Pauli principle. The origin of periodicity in the properties of elements then becomes obvious. The orbital energy pattern and the Pauli principle are, therefore, crucial for understanding the structure of the periodic table.

To follow why and how the energy level scheme of the hydrogen atom gets modified in a multi-electron situation, we consider the ground state distribution of electrons in the atoms of three elements—hydrogen, helium and lithium which have one, two and three electrons respectively. In hydrogen, the electron goes in the lowest energy orbital, $1s$, say with an 'up' spin. This orbital can accommodate the second electron of helium, only if it has opposite spin. If the two electrons have the same spin, the three orbital quantum numbers as well as the spin quantum number would be identical, a situation that is prohibited by the Pauli principle. Thus, there being no place in the $1s$ orbital for further electrons, the third electron of lithium has to occupy the next higher energy orbital. Should the third electron be placed in the $2s$ or $2p$ orbital? If the hydrogen atom energy level pattern were valid for multi-electron atoms, it makes no difference since they all have equal energy. But it turns out that in lithium the $2s$ orbital has lower energy than the $2p$ orbital for the following reason. We have already seen that the maxima of the $2s$ and $2p$ orbitals are at distances greater than the $1s$ maximum. Therefore, an electron in the $2s$ or the $2p$ orbital in lithium will be outside the two $1s$-electrons. The third electron will not experience attraction due to the full nuclear charge because
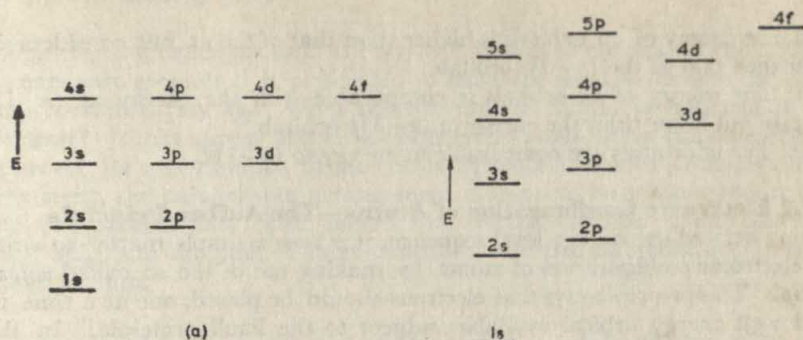
Fig. 3.46 The energy level diagram valid for (a) the hydrogen atom and (b) multi-electron atoms

of the shielding effect of the inner $1s$ electrons. However, the shielding felt by a $2s$ electron is less than that felt by a $2p$ electron, since the $2s$ orbital penetrates closer to the nucleus where there is no shielding. This means that a $2s$ electron experiences comparatively more attraction from the nucleus than a $2p$ electron (i.e. a $2s$ electron is more tightly bound than a $2p$ electron). The $2s$ orbital therefore has lower energy than the $2p$ orbitals.

In general, orbitals with the same value of n but different values of l do not have the same energy in multi-electron atoms. Within a set of orbitals with a particular value of n, the energy increases as l increases. This is because as the value of l increases, the orbital penetration near the nucleus decreases and the shielding due to inner electrons becomes more effective; in other words, an electron with large l value feels less nuclear charge. The energy level pattern
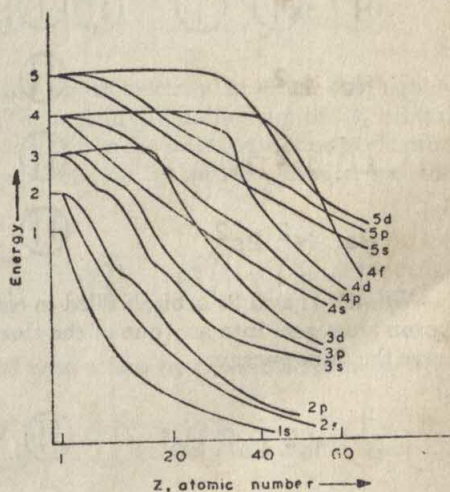
Fig. 3.47 The variation of orbital energies with the atomic number (Z)

which is qualitatively valid for nearly all multi-electron atoms is given in Fig. 3.46(b). The variation of orbital energies with atomic number is shown in Fig. 3.47. The variation of orbital energies is summarised as:

(*i*) The energy of np orbitals is higher than that of the ns, but considerably lower than that of the $(n+1)s$ orbitals.

(*ii*) The energy of nd orbitals is comparable with the energy of $(n+1)s$ orbitals, but lower than the energy of $(n+1)p$ orbitals.

(*iii*) The nf orbitals are comparable in energy to $(n+1)d$.

3.11.2 Electronic Configuration of Atoms—The Aufbau Principle

Having derived the energy level sequence, it is now a simple matter to write the electronic configuration of atoms, by making use of the so called *aufbau principle*. This principle says that electrons should be placed, one at a time, in the lowest energy orbital available, subject to the Pauli principle. In the hydrogen atom, the only electron is in the $1s$ orbital, the second electron in helium also going in the same orbital but with opposite spin (He, $1s^2$). The completion of $1s$ orbital marks the end of the first period. The next electron has to occupy the $2s$ orbital as in lithium (Li, $1s^2 2s^1$). This orbital can accommodate another electron with the opposite spin as in beryllium (Be, $1s^2 2s^2$).

It is convenient at this stage to introduce a notation for indicating electronic configurations. We will represent orbitals by circles, an empty circle representing an unoccupied orbital. A single electron in an orbital will be shown by drawing an arrow and a pair of electrons (the maximum number which an orbital can accommodate) by drawing two arrows. The arrow head will signify the ' up ' or ' down ' orientation of the electron spin. In terms of this notation, the configurations of the atoms discussed above can be written as follows:

		1s	2s	2p		
H	$1s^1$	↑	○	○	○	○
He	$1s^2$	↑↓	○	○	○	○
Li	$1s^2\ 2s^1$	↑↓	↑	○	○	○
Be	$1s^2\ 2s^2$	↑↓	↑↓	○	○	○
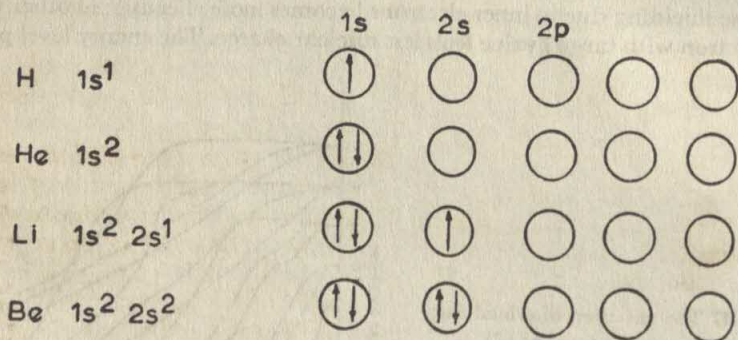
With the $1s$ and $2s$ orbitals filled to capacity, the additional electron in the boron atom goes into any one of the three $2p$ orbitals (say $2p_x$) all of which have the same energy.

B	$1s^2\ 2s^2\ 2p^1$	↑↓	↑↓	↑	○	○
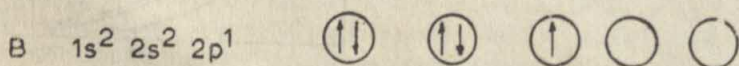
If the sixth electron of the carbon atom is placed in the $2p_x$ orbital, then this pair of electrons will occupy the same region of space but if the additional electron is placed in either of the empty $2p_y$ or $2p_z$ orbitals, then the two electrons will occupy different regions of space. It is obvious that electron

repulsion, and hence the total energy, will be less in the second case. Thus, on energetic grounds it is preferable to assign the sixth electron to one of the empty orbitals (say $2p_y$). What spin orientation should be assigned to this electron? It may appear that either orientation should have the same energy. However, for reasons which cannot be easily explained in a non-mathematical treatment, the parallel spin arrangement is found to have lower energy than the anti-parallel one. This means that the $2p_y$ electron should also have 'up' spin. On the basis of these considerations, the configuration of carbon atom becomes

C $1s^2 2s^2 2p^2$ (↑↓) (↑↓) (↑) (↑) ◯

Since we shall be meeting cases similar to the carbon atom, it is useful to generalise the arguments given above in the form of two rules, known as *Hund's rules*.

(*i*) In filling a group of orbitals of equal energy, it is energetically preferable to assign electrons to empty orbitals rather than pair them in a particular orbital.
(*ii*) When two electrons are placed in two different orbitals, energy is lower if the spins are parallel.

Using the two rules, it is easy to see that nitrogen atom should have the configuration:

N $1s^2 2s^2 2p^3$ (↑↓) (↑↓) (↑) (↑) (↑)

In the oxygen atom, we can place the eighth electron in either the higher-energy empty $3s$ orbital with an 'up' spin or in the half-occupied $2p_x$ orbital with 'down' spin. Since the energy increase in the latter case (due to electron repulsion) is less than the energy gap between $2p$ and $3s$, oxygen has the configuration:

O $1s^2 2s^2 2p^4$ (↑↓) (↑↓) (↑↓) (↑) (↑)

The configurations of the fluorine and neon atoms by the same reasoning are:

F $1s^2 2s^2 2p^5$ (↑↓) (↑↓) (↑↓) (↑↓) (↑)

Ne $1s^2 2s^2 2p^6$ (↑↓) (↑↓) (↑↓) (↑↓) (↑↓)
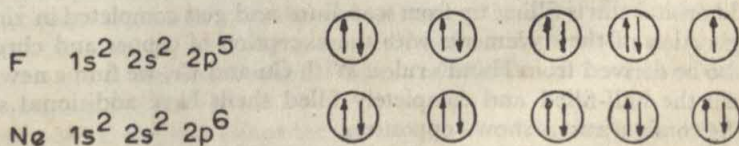
The K and L shells get filled up in neon. So starting wih sodium, the electrons are assigned in the M shell. The electron configurations of the elements

from sodium to argon can be derived from exactly the same considerations as given above.

		3s	**3p**		
Na	$3s^1$	↑	○	○	○
Mg	$3s^2$	↑↓	○	○	○
Al	$3s^2\,3p^1$	↑↓	↑	○	○
Sc	$3s^2\,3p^2$	↑↓	↑	↑	○
P	$3s^2\,3p^3$	↑↓	↑	↑	↑
S	$3s^2\,3p^4$	↑↓	↑↓	↑	↑
Cl	$3s^2\,3p^5$	↑↓	↑↓	↑↓	↑
Ar	$3s^2\,3p^6$	↑↓	↑↓	↑↓	↑↓

We have shown above only the unfilled shell, also commonly called as the valence shell. The completely-filled shells (closed shells) have been left out for the sake of brevity.

In potassium and calcium, the 4s orbital—which is lower in energy than the 3d orbital—gets filled first. Their configurations are:

		4s	**3d**				
K	$4s^1$	↑	○	○	○	○	○
Ca	$4s^2$	↑↓	○	○	○	○	○

The 3d orbital starts filling up from scandium and gets completed in zinc. The configuration of these elements with the exception of copper and chromium, can also be derived from Hund's rules. With Cu and Cr, we find a new feature wherein the half-filled and completely filled shells have additional stability (see the configurations shown opposite).

With the saturation of the 3d orbitals, the 4p orbitals start getting filled from gallium to krypton. In the next eighteen elements from rubidium to xenon, the pattern of filling the 5s, 4d, and 5p orbitals is exactly analogous to

		4 s	3 d				
Sc	$4s^2\,3d^1$	⇅	↑	○	○	○	○
Ti	$4s^2\,3d^2$	⇅	↑	↑	○	○	○
V	$4s^2\,3d^3$	⇅	↑	↑	↑	○	○
Cr	$4s^1\,3d^5$	↑	↑	↑	↑	↑	↑
Mn	$4s^2\,3d^5$	⇅	↑	↑	↑	↑	↑
Fe	$4s^2\,3d^6$	⇅	⇅	↑	↑	↑	↑
Co	$4s^2\,3d^7$	⇅	⇅	⇅	↑	↑	↑
Ni	$4s^2\,3d^8$	⇅	⇅	⇅	⇅	↑	↑
Cu	$4s^1\,3d^{10}$	↑	⇅	⇅	⇅	⇅	⇅
Zn	$4s^2\,3d^{10}$	⇅	⇅	⇅	⇅	⇅	⇅

the $4s$, $3d$ and $4p$ case discussed above. Then comes the turn of the $6s$ orbital and in cesium and barium this orbital contains one and two electrons respectively. After one electron has entered $5d$ in lanthanum, the seven $4f$ orbitals being next in the order of increasing energy are available for occupation. These get filled completely in ytterbium. We have then progressive filling of $5d$, then $6p$, then $7s$ and finally $5f$ orbitals. The elements after uranium are all short-lived and all of them are produced artificially. The electronic configurations of all the atoms is given in Table 3.4. The detailed orbital distribution of electrons in a given atom can be worked out in the same manner as has been done above for the atoms up to zinc.

It may be pointed out that the electronic configuration of an atom is deduced from analysis of atomic spectra and of magnetic data. For many atoms, especially the heavier ones, the spectra are quite complicated and the assignment of electrons becomes doubtful. We have indicated such cases in the Table 3.4 by putting a (?) mark.

A few general remarks about the meaning of some of the terms used in this section are in order. Statements like ‘ an electron is placed in an orbital ’, or ‘ an orbital is getting filled ’ or ‘ electrons occupy certain orbitals ’ should not

Table 3.4 Ground State Electron Configuration of Atoms

Z	Element	1	2		3			4				5				6				7
		s	s	p	s	p	d	s	p	d	f	s	p	d	f	s	p	d	f	s
1	H	1																		
2	He	2																		
3	Li	2	1																	
4	Be	2	2																	
5	B	2	2	1																
6	C	2	2	2																
7	N	2	2	3																
8	O	2	2	4																
9	F	2	2	5																
10	Ne	2	2	6																
11	Na	2	2	6	1															
12	Mg	2	2	6	2															
13	Al	2	2	6	2	1														
14	Si	2	2	6	2	2														
15	P	2	2	6	2	3														
16	S	2'	2	6	2	4														
17	Cl	2	2	6	2	5														
18	Ar	2	2	6	2	6														
19	K	2	2	6	2	6		1												
20	Ca	2	2	6	2	6		2												
21	Sc	2	2	6	2	6	1	2												
22	Ti	2	2	6	2	6	2	2												
23	V	2	2	6	2	6	3	2												
24	Cr	2	2	6	2	6	5	1												
25	Mn	2	2	6	2	6	5	2												
26	Fe	2	2	6	2	6	6	2												
27	Co	2	2	6	2	6	7	2												
28	Ni	2	2	6	2	6	8	2												
29	Cu	2	2	6	2	6	10	1												
30	Zn	2	2	6	2	6	10	2												
31	Ga	2	2	6	2	6	10	2	1											
32	Ge	2	2	6	2	6	10	2	2											
33	As	2	2	6	2	6	10	2	3											
34	Se	2	2	6	2	6	10	2	4											
35	Br	2	2	6	2	6	10	2	5											
36	Kr	2	2	6	2	6	10	2	6											
37	Rb	2	2	6	2	6	10	2	6			1								
38	Sr	2	2	6	2	6	10	2	6			2								
39	Y	2	2	6	2	6	10	2	6	1		2								
40	Zr	2	2	6	2	6	10	2	6	2		2								

Table 3.4 (Contd.)

Z	Element	1	2		3			4				5				6				7
		s	s	p	s	p	d	s	p	d	f	s	p	d	f	s	p	d	f	s
41	Nb	2	2	6	2	6	10	2	6	4		1								
42	Mo	2	2	6	2	6	10	2	6	5		1								
43	Tc	2	2	6	2	6	10	2	6	6		1?								
44	Ru	2	2	6	2	6	10	2	6	7		1								
45	Rh	2	2	6	2	6	10	2	6	8		1								
46	Pd	2	2	6	2	6	10	2	6	10										
47	Ag	2	2	6	2	6	10	2	6	10		1								
48	Cd	2	2	6	2	6	10	2	6	10		2								
49	In	2	2	6	2	6	10	2	6	10		2	1							
50	Sn	2	2	6	2	6	10	2	6	10		2	2							
51	Sb	2	2	6	2	6	10	2	6	10		2	3							
52	Te	2	2	6	2	6	10	2	6	10		2	4							
53	I	2	2	6	2	6	10	2	6	10		2	5							
54	Xe	2	2	6	2	6	10	2	6	10		2	6							
55	Cs	2	2	6	2	6	10	2	6	10		2	6			1				
56	Ba	2	2	6	2	6	10	2	6	10		2	6			2				
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2				
58	Ce	2	2	6	2	6	10	2	6	10	2	2	6			2?				
59	Pr	2	2	6	2	6	10	2	6	10	3	2	6			2?				
60	Nd	2	2	6	2	6	10	2	6	10	4	2	6			2				
61	Pm	2	2	6	2	6	10	2	6	10	5	2	6			2?				
62	Sm	2	2	6	2	6	10	2	6	10	6	2	6			2				
63	Eu	2	2	6	2	6	10	2	6	10	7	2	6			2				
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2				
65	Tb	2	2	6	2	6	10	2	6	10	9	2	6			2?				
66	Dy	2	2	6	2	6	10	2	6	10	10	2	6			2?				
67	Ho	2	2	6	2	6	10	2	6	10	11	2	6			2?				
68	Er	2	2	6	2	6	10	2	6	10	12	2	6			2?				
69	Tm	2	2	6	2	6	10	2	6	10	13	2	6			2				
70	Yb	2	2	6	2	6	10	2	6	10	14	2	6			2				
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2				
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2				
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2				
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4		2				
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2				
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2				
77	Ir	2	2	6	2	6	10	2	6	10	14	2	6	7		2				
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1				
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1				
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2				
81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1			
82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2			
83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3			
84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4?			
85	At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5?			

Table 3.4 (Contd.)

Z	Element	1	2	3	4	5	6	7
		s	$s\ p$	$s\ p\ d$	$s\ p\ d\ f$	$s\ p\ d\ f$	$s\ p\ d\ f$	s
86	Rn	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	
87	Fr	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	.1?
88	Ra	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	2
89	Ac	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 1	2?
90	Th	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 2	2
91	Pa	2	2 6	2 6 10	2 6 10 14	2 6 10 2	2 6 1	2?
92	U	2	2 6	2 6 10	2 6 10 14	2 6 10 3	2 6 1	2
93	Np	2	2 6	2 6 10	2 6 10 14	2 6 10 4	2 6 1	2?
94	Pu	2	2 6	2 6 10	2 6 10 14	2 6 10 6	2 6	2?
95	Am	2	2 6	2 6 10	2 6 10 14	2 6 10 7	2 6	2?
96	Cm	2	2 6	2 6 10	2 6 10 14	2 6 10 7	2 6 1	2?
97	Bk	2	2 6	2 6 10	2 6 10 14	2 6 10 8	2 6 1	2?
98	Cf	2	2 6	2 6 10	2 6 10 14	2 6 10 10	2 6	2?
99	Es	2	2 6	2 6 10	2 6 10 14	2 6 10 11	2 6	2?
100	Fm	2	2 6	2 6 10	2 6 10 14	2 6 10 12	2 6	2?
101	Md	2	2 6	2 6 10	2 6 10 14	2 6 10 13	2 6	2?
102	No	2	2 6	2 6 10	2 6 10 14	2 6 10 14	2 6	2?
103	Lw	2	2 6	2 6 10	2 6 10 14	2 6 10 14	2 6 1	2?

be interpreted to mean that orbitals are some kind of 'containers'. What is meant by these statements is that the behaviour of an electron in an atom is characterised by a set of quantum numbers, which in turn characterise a particular atomic orbital. In this sense an orbital exists physically only if an electron 'occupies' it. It should also be clearly understood that an orbital does not have fixed energy. The energy of an orbital depends not only on the nuclear charge but also on the inter-electron repulsion. Consequently, when an atom ionises, the orbital energy pattern may change due to changes in the electron population and electron-repulsion effects. This happens if the approximate energies of two orbitals are comparable. For example, from scandium to copper, the $4s$ orbital is occupied before the $3d$ (i.e. $4s$ is lower than $3d$) in the filling process, but the $4s$ electrons are lost before the $3d$ ones in the ionisation process (i.e. $3d$ is lower than $4s$). In other words, the energy level diagram for an atom and for its ions need not always be the same.

3.12 CORRELATION OF ATOMIC BEHAVIOUR WITH ATOMIC STRUCTURE

One of the great merits of the modern atomic theory lies in its ability to interpret atomic behaviour in terms of the electronic structure of atoms. In this section, we shall examine the connection between the electronic configuration and the periodic variation in the properties of the elements. We shall then briefly discuss the connection between electronic structure and magnetism.

3.12.1 Modern Periodic Law

The original periodic law (Chapter 2) stated that the properties of the elements and their compounds are a periodic function of the atomic mass. However, the periodic table built on this law showed some inconsistencies. For example, in three pairs of elements, argon and potassium, nickel and cobalt, and tellurium and iodine, the ordering based on atomic mass had to be reversed arbitrarily to suit experimental facts. When the structure of an atom became established and it was possible to determine the atomic numbers accurately (see section 3.2), it was realised that if the elements were arranged in order of increasing atomic numbers rather than atomic masses, these anamolies disappeared. Consequently, the periodic law was revised and it now states that *the properties of the elements and their compounds are a periodic function of the atomic number*. The modern periodic table is based on this form of the law.

3.12.2 Long Form of the Periodic Table

The most popular version of the periodic table in use today is the long form shown in Table 3.5. In this form, the elements fall into eighteen columns. To keep the table from being too drawn out, the fourteen elements which follow lanthanum and the fourteen elements which follow actinium are placed in separate rows at the bottom of the table. Elements belonging to the same column are said to comprise a *family or group*. The six inert elements (noble gases) in the extreme right-hand column are designated as the zero group. With the solitary exception of the three columns (containing nine elements) towards the centre of the table which are collectively known as the VIII group, all the other fourteen columns belong to either the *A* sub-group or *B* sub-group of the seven parent groups. The rationale behind this labelling is as follows. The elements of a particular sub-group show very strong chemical resemblance to each other, but kinship also exists between them and the elements of the other sub-group of the same parent group. For example, the six elements of the alkaline earth family (group IIA) not only exhibit similar chemical behaviour, but also show considerable resemblance to the three elements of the group IIB.

Having brought out the significance of (vertical) group classification, we turn to the significance of (horizontal) rows. The elements within a row (sometimes called a *period*) show gradual variation of behaviour which means that a particular element exhibits some similarity with its neighbours, but appreciable dissimilarity with its non-neighbours. These vertical–horizontal characteristics of the periodic table result in the fact that the table can be 'read' like a crossword puzzle. In addition, the periodic 'puzzle' contains at many places diagonal patterns which also illuminate physico-chemical behaviour.

3.12.3 Electronic Configuration and Major Types of Elements

From the configuration point of view, the periodic table separates out into blocks of elements in which the s, p, d and f orbitals are filled up. One can further classify all the elements on this basis into four general types.

Inert (or Noble) elements: These constitute the zero group. They are all characterised by a completely filled outer shell with the configuration ns^2np^6, helium being an exception. Helium also has a completely filled outer shell but the configuration is $1s^2$. The extra-stable configuration of these elements cannot be easily altered by either electron addition or electron removal.

Table 3.5 Long Form of the Periodic Table

s block		d block										p block					zero group
s^1 IA	s^2 IIA	d^1 IIIB	d^2 IVB	d^3 VB	d^4 VIB	d^5 VIIB	d^6 VIII	d^7 VIII	d^8 VIII	d^9 IB	d^{10} IIB	p^1 IIIA	p^2 IVA	p^3 VA	p^4 VIA	p^5 VIIA	
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 ● La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 ● Ac	103														

4f ●	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
5f ●	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

☐ Metals ▨ Non-metals ▨ Rare gases

These elements are thus usually unreactive though under special conditions, some of them can be induced to form compounds (see Chapter 16 for noble gas compounds).

Representative elements: All the elements of the s- and p-block, with the exception of inert elements, belong to this category (see Chapter 16 for the chemistry of these elements). They all have incomplete outermost shells. The electronic configuration varies from ns^1 through ns^2np^5. For example, the elements of group IA have an incomplete s-level (configuration ns^1), the elements of group IIA have a completed s sub-shell (configuration ns^2), while the elements of groups III to VII have partially filled p-levels (configuration np^1 to np^5). Representative elements attain the stable ns^2np^6 configuration by entering into chemical combination through losing, gaining, or sharing electrons.

Transition elements: These elements have two outermost incomplete shells with the general configuration $(n-1)d^{1-9}ns^{1 \text{ or } 2}$. There are three transition series corresponding to the unfilled $3d$, $4d$, and $5d$ orbitals. The elements in this class show striking resemblance to each other, e.g. form coloured ions, have several valence states, form coordination compounds and so on (see Chapter 17).

Inner transition elements: The elements of this type are similar to the transition elements, but differ from the regular transition elements in that they have three outermost shells which are incomplete. They are known as inner transition elements, inasmuch as they not only have incomplete d-levels but also, incomplete f-levels. Inner transition elements comprise two series, the lanthanides, in which the $4f$ level gets filled up, and the actinides, in which the $5f$ level gets filled up (see Chapters 17 and 19).

Our classification clearly brings out the fact that there is a close connection between electronic structure and the chemical behaviour of elements. Thus, all the inert gases have similar electronic structures with completely filled ns and np orbitals and they behave alike chemically. Similarly, chemically similar alkali metals have a single s electron outside the closed shell. All halogens have ns^2np^5 electronic configuration, while oxygen, sulphur and selenium with strong chemical resemblance to each other have the configuration $2p^4$, $3p^4$ and $4p^4$ respectively. The metal–non-metal classification also shows correlation with electronic structure. Most metals (e.g. Na, Be, Al) have one to three more electrons, while most non-metals (e.g. F,O,N) have one to three less electrons, compared to the closed-shell configurations. The similarity of chemical behaviour amongst lanthanides and amongst actinides is also understandable, as the outer orbital structure in each of these groups is the same, differences existing only in the inner $4f$- and $5f$-levels. The same explanation holds for the three transition series where the differences are only in the number of d electrons. We conclude, therefore, that (a) outer electronic structure controls chemical behaviour, (b) similarity in electronic configuration is responsible for family resemblance amongst elements, and (c) similarity in configurations, and hence periodicity, arises because of the energy level pattern of orbitals and the Pauli exclusion principle.

3.12.4 Periodic Properties
A very large number of physical and chemical properties of the elements vary periodically with atomic number. Properties like ionisation energy and electron affinity, which belong to individual atoms, are connected to the electronic configuration in a very direct manner. Their periodic variation with atomic number can be explained in great detail as is shown below. Properties like density, melting point, or atomic volume, on the other hand, belong to a collection of atoms (bulk properties) and their connection to the electronic configuration is indirect. We shall only summarise here their periodic variation. Then, there are properties like electronegativity and atomic size which depend on the environment of an atom and which, therefore, are not strictly invariant atomic properties. Their periodic behaviour is discussed in Chapter 4. Finally, the periodicity of chemical properties such as oxidation states, and behaviour of oxides and hydrides are discussed separately for some representative elements (Chapter 16), and transition elements and inner-transition elements (Chapter 17).

Ionisation energy: Ionisation energy (IE) of an atom is the energy required to remove one electron from the atom. The energy needed to pull the first electron is called the first ionisation energy (IE_1) while the energies needed to remove the second, third and further electrons are designated as the second ionisation energy (IE_2), the third ionisation energy (IE_3) and so on. Ionisation energies are experimentally determinable quantities. They are readily obtained from the spectra of the gaseous species or alternatively by subjecting the gas at low pressure to external voltage. As the voltage is increased, the gas starts conducting (due to ionisation) at a definite value of the voltage; from this value, the value of IE can be calculated.

The ionisation energies of various elements are given in Table 3.6 and the variation of the first ionisation energy with atomic number, Z, is shown in Fig. 3.48. The trends in the ionisation energy values can be easily understood on the basis of electronic structure.
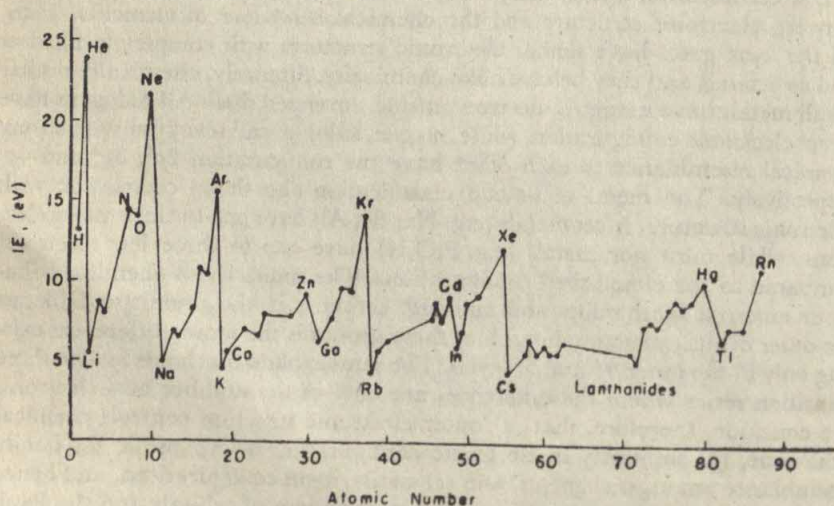
Fig. 3.48 The variation of the first ionisation energy with the atomic number (Z)

For all elements, the successive values of ionisation energy increase. This is due to the fact that the removal of each electron increases the positive charge on the atom by one. Thus, successive electrons have to be removed from ions with increasing positive charge—a process that naturally requires more and more energy. The understanding of the periodic variation of ionisation energy (say IE_1) with atomic number involves a detailed consideration of electronic distribution.

It is obvious that the most loosely held electron will be the first one to be removed. Now the attractive forces an electron experiences in an atom are directly proportional to the net nuclear charge it feels and are inversely proportional to the square of the distance between the electron and the nucleus. The net nuclear charge is the actual nuclear charge (as given by the atomic number, Z, minus the shielding due to the inner electrons) while the distance (meaning average distance) depends on the type of orbital the electron is occupying. Thus, the variation in the ionisation energy is related to (a) the actual nuclear charge Z, (b) the extent of shielding by the inner electrons, and

Table 3.6 First Ionisation Energies (IE_1) of Elements

Element	Atomic No.	IE_1 (ev)	Element	Atomic No.	IE_1 (ev)	Element	Atomic No.	IE_1 (ev)
H	1	13·6	Ge	32	8·1	Eu	63	5·7
He	2	24·6	As	33	9·8	Gd	64	6·2
Li	3	5·4	Se	34	9·8	Tb	65	6·7
Be	4	9·3	Br	35	11·8	Dy	66	6·8
B	5	8·3	Kr	36	14·0	Ho	67	—
C	6	11·3	Rb	37	4·2	Er	68	—
N	7	14·5	Sr	38	5·7	Tm	69	—
O	8	13·6	Y	39	6·4	Yb	70	6·2
F	9	17·4	Zr	40	6·8	Lu	71	5·0
Ne	10	21·6	Nb	41	6·9	Hf	72	7·0
Na	11	5·1	Mo	42	7·1	Ta	73	7·9
Mg	12	7·6	Te	43	7·3	W	74	8·6
Al	13	6·0	Ru	44	7·4	Re	75	7·9
Si	14	8·2	Rh	45	7·5	Os	76	8·7
P	15	11·0	Pd	46	8·3	Ir	77	9·0
S	16	10·4	Ag	47	7·6	Pt	78	9·0
Cl	17	13·0	Cd	48	9·0	Au	79	9·2
Ar	18	15·8	In	49	5·8	Hg	80	10·4
K	19	4·3	Sn	50	7·3	Tl	81	6·1
Ca	20	6·1	Sb	51	8·6	Pb	82	7·4
Sc	21	6·5	Te	52	9·0	Bi	83	7·3
Ti	22	6·8	I	53	10·5	Po	84	8·4
V	23	6·7	Xe	54	12·1	At	85	—
Cr	24	6·8	Cs	55	3·9	Rn	86	10·7
Mn	25	7·4	Ba	56	5·2	Fr	87	—
Fe	26	7·9	La	57	5·6	Ra	88	5·3
Co	27	7·9	Ce	58	6·9	Ac	89	6·9
Ni	28	7·6	Pr	59	5·8	Th	90	—
Cu	29	7·6	Nd	60	6·3	Pa	91	—
Zn	30	9·4	Pm	61	—	U	92	4·0
Ga	31	6·0	Sm	62	5·6			

(*c*) the nature of the orbital which controls the average distance from the nucleus.

The increase in IE_1 from hydrogen ($Z=1$) to helium ($Z=2$) is due to increase in nuclear charge. The drop in the IE_1 of lithium results in spite of the increase in $Z(Z=3)$ because the inner two 1s-electrons shield the nucleus and, also because the average distance of the 2s electron is greater. The increase in beryllium is again due to increase in Z. The slight decrease in boron may seem surprising since Z has increased while the 2p electron distance is about the same as 2s electron distance. The reason here is the smaller penetration of the 2p electron which is, therefore, more effectively shielded by the inner electrons. Hence, though the actual nuclear charge has increased, the net nuclear charge as experienced by the 2p electron has decreased causing the drop in IE_1 of boron. The values for carbon and nitrogen increase due to the increasing Z. In nitrogen the three electrons in 2p orbital occupy $2p_x$, $2p_y$ and $2p_z$ orbitals to minimise the electron repulsion. In oxygen, the additional electron has to be placed in one of the p orbitals which already has an electron in it. The increased repulsion counter-balances the effect of Z thus slightly lowering the IE_1 for oxygen. The monotonic increase of IE_1 up to neon is again due to the increasing nuclear charge. The variations in the other elements can be rationalised in a similar manner.

The variation of ionisation energy can be summarised as follows: (*a*) Along any row, the ionisation energy tends to increase with atomic number. (*b*) Down a column, the ionisation energy decreases with atomic number. This is particularly clear amongst the representative elements, and it is responsible for bunching of elements with low ionisation energy in the lower left-hand corner and the elements with high ionisation energy in the upper right-hand corner of the periodic table. Since low ionisation energy facilitates the formation of the metallic bond (Chapter 7), the metallic character of elements increases progressively within a family as the atomic number increases. Conversely, the non metallic character is dominant in the lighter elements in every family. Both these features can be supported by several examples. In group IA, the lightest element, hydrogen, is a non-metal but the rest are metals while in group IIA there are no non-metals. In group IIIA, boron is a semi-metal, the remaining elements being metals. Similar trends exist in groups IVA–VIIA.

Electron affinity: The electron affinity (EA) of an atom is the energy change resulting from the addition of an electron to the neutral gaseous atom. A positive EA indicates that the negative ion is more stable than the neutral atom whereas a negative EA means the opposite. Electron affinity is rather difficult to measure and only limited experimental data are available (see Table 3.7).

Table 3.7 Electron Affinities of Some Elements

Symbol	Electron Affinity		Symbol	Electron Affinity	
	Kcal	ev		Kcal	ev
F	98·5	4·27	O	−168[1]	−7.28[1]
Cl	92·5	4·01	S	− 79·4[1]	−3.44[1]
Br	87.1	3·78	Se	− 97[1]	−4·21[1]
I	79·2	3·43	Li–Cs	0	0
H	16·4	0·71			

[1]For two electrons

The halogens have by far the largest electron affinities. The reason for this is that halogens are only one electron short of the highly stable inert gas configurations. Although the additional electron increases the electron repulsion, the effect is more than compensated for by the extra stability of closed-shell configuration. The positive EA's in the oxygen family are explicable in the same manner.

Electron affinity values reinforce the metal–non-metal classification. The non-metals in the upper right-hand corner have high electron affinities and, therefore, they have less tendency to lose electrons than do the metals and semi-metals.

Atomic volume: The atomic volume is defined as the volume occupied by a gram mole of an element; it is the atomic mass divided by the density, or the volume occupied by $6 \cdot 02 \times 10^{23}$ atoms of an element. Therefore, the atomic volumes of the elements should be the volumes occupied by the same number of atoms. In Fig. 3.49 atomic volumes of elements are plotted against atomic numbers. The plot shows the following features: (*a*) the curve is a succession of waves, the crests of which are occupied by the alkali metals, and the troughs by relatively unreactive and infusible elements; (*b*) the ascending portions of the curve are occupied by electronegative elements (that is mainly non-metals); (*c*) the descending portions are occupied by electropositive elements (that is mainly metals); and (*d*) adjacent to the trough of the wave, occur some brittle metals, whilst in the space between these two portions fall malleable metals.
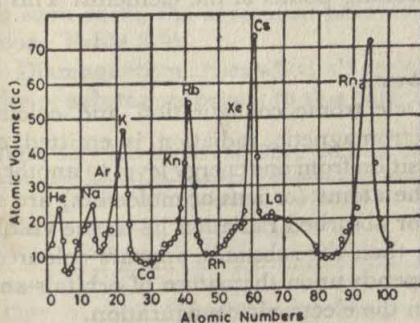
Fig. 3.49 Periodicity of atomic volumes

Fig. 3.51 Periodicity of melting points

Fig. 3.50 Periodicity of densities
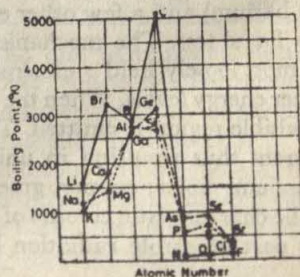
Fig. 3.52 Periodicity of boiling points

Density: The densities of elements in the solid state vary periodically with their atomic numbers as shown in Table 3.8. The periodicity varies in a regular

Table 3.8 Densities of Some Elements

Na	Mg	Al	Si	P	S	Cl[1]
0·97	1·74	2·74	2·42	2·20	2·07	1·51
K	Ca	Sc	Ti	V	Cr	Mn
0·87	1·54	2·4	4·5	4·96	6·92	7·42
Fe	Co	Ni	Cu	Zn	Ga	Ge
7·8	8·9	8·9	8·93	7·15	5·91	5·47
		As	Se	Br[1]		
		5·73	4·8	2·97		

[1]Densities in liquid state

manner from member to member within a period and reaches a maximum for the central members. The change in density with atomic number for the lighter elements is indicated graphically in Fig. 3.50.

Melting and boiling points: In Fig. 3.5[1], the melting points of some elements are plotted against their atomic numbers. From this plot, we see that melting point is minimum in the noble gases and maximum in group IV (for the lighter elements) and group VI (for the heavier elements) elements. Also, the members of the same family of elements occupy similar positions on the ascending or descending portion of the curve.

Similar periodicity is shown by the boiling points of the elements. This is depicted in Fig. 3.52.

3.12.5 Electronic Structure and Colour

There is a direct connection between electronic configuration and colour. As has been pointed out earlier, electromagnetic radiation is emitted or absorbed when an electron makes a transition from one energy level to another. If in a substance the energy levels of the atoms (or ions or molecules) are so spaced that the wavelengths of emitted or absorbed radiation lie in the visible region of the electromagnetic spectrum, then the substance appears coloured. The energy level spacing, of course, depends upon the nature of orbitals and because of this, the colour depends upon the electronic configuration.

In atoms, the colour is usually due to the emission process. For example, all the alkali elements, some of the alkaline earths (e.g. calcium, strontium, and barium) and a few other elements (e.g. copper) give characteristic colours in a flame test. The mechanism of this is as follows. Thermal energy excites the most loosely held s electron in the atoms of these elements to one of the higher energy levels. When the electron returns to the ground level, radiation in the visible region is emitted. The magnitude of energy gap in each element is different thus resulting in unique colours (e.g. sodium gives yellow colour; potassium, violet; copper, green).

The characteristic colours of *coordination compounds** are due to the absorption of a part of visible radiation by the metal ion present in these compounds.

*Coordination compounds are discussed in Chapter 17.

The energies of the five d-orbitals in an isolated metal atom or an isolated ion are equal, but in coordination compounds, the energies of the d orbitals of the metal ion are not equal.* The resulting energy gap corresponds to wavelengths in the visible region. Consequently, when white light is incident on such compounds a part of the visible portion is absorbed and the rest is transmitted thus conferring a characteristic colour on the compound. The colour in molecules is also due to absorption. This topic is discussed further in Chapter 4.

3.12.6 Electronic Structure and Magnetism

The magnetic behaviour of substances is also a direct consequence of the electronic structure. There are three types of magnetic substances: (a) *paramagnetic* (those that are attracted into magnetic fields), (b) *diamagnetic* (those that are repelled by magnetic fields), and (c) *ferromagnetic* (those that are strongly attracted into the magnetic fields).

Paramagnetism arises if the atoms, ions or molecules comprising the substance have a net magnetic moment. This happens whenever one or more unpaired electrons are present in the system (e.g. H atom, Cu^{2+} ion, O_2 molecule). Consequently, paramagnetism can be predicted from electronic structure. One can even calculate the magnetic moment due to the unpaired spins (see section 3.10.1). However, for free atoms, agreement with experiment is not good because orbital angular momentum also makes contribution to the magnetic moment. The theory which takes this into account is rather complex and is outside the scope of this book. However, in many compounds of transition metal ions, it can be shown that the orbital angular momentum vanishes and that the magnetic moment is entirely due to the spin of the parent ion. In such cases, the agreement between calculated and observed values is very good (Table 3.9).

Diamagnetism arises when all the electrons are paired (e.g. He, N_2). Majority of substances belong to this category.

Table 3.9 Calculated and Observed Magnetic Moments of Some Ions

Ion	Number of unpaired electrons	Calculated moment (BM)	Observed moment (BM)	Ion	Number of unpaired electrons	Calculated moment (BM)	Observed moment (BM)
V^{4+}	1	1·73	1·7–1·8	Co^{2+}	3	3·87	4·1–5·2
Cu^{2+}	1	1·73	1·7–2·2	Fe^{2+}	4	4·90	5·1–5·5
V^{3+}	2	2·83	2·6–2·8	Co^{2+}	4	4·90	5·4
Ni^{2+}	2	2·83	2·8–4·0	Mn^{2+}	5	5·92	5·9
Cr^{3+}	3	3·87	3·8	Fe^{3+}	5	5·92	5·9

Ferromagnetism, like paramagnetism, is also due to unpaired electrons. However, unlike paramagnetism, it is a bulk property. Ferromagnetic materials (a common example is the familiar magnet) are very important in technology. Ferromagnetism will be dealt with briefly in Chapter 7.

There are several other properties, apart from colour and magnetism, which are linked to electronic structure. However, the link in many of such cases is rather indirect. In the chapters that follow, we shall point out the correlation between the properties and electron behaviour, wherever feasible.

*See Chapters 4 and 17 for an explanation of this effect.

SUGGESTED READING

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PROBLEMS

3.1 Calculate the number of electrons which together will weigh one gram.

3.2 Calculate the mass of one mole of electron.

3.3 Compare the e/m for the following pairs: (a) Li^+ and Na^+ and (b) Li^+ and Be^{2+}.

3.4 (a) The radius of the hydrogen atom nucleus is (approximately) 10^{-13} cm. The average radius of the hydrogen atom is 0.5×10^{-8} cm. Calculate the radius ratio. Name two objects on macroscopic scale which have similar radius ratio. (b) Assuming the nucleus and atom as perfect spheres, calculate the volume ratio.

3.5 Calculate the density of nuclear matter in hydrogen atom.

3.6 Calculate the charge density (in coulomb/cc) if a unit positive charge $(1.6 \times 10^{-19}$ coulomb) is spread over (a) the whole atom and (b) the nucleus only.

3.7 (a) State the assumptions Bohr made about the motion of an electron around a nucleus. (b) In his theory of the hydrogen atom, what equation did Bohr give, relating electrostatic force on the electron to the acceleration of the electron in its orbit? (c) Calculate the energy of the lowest energy state from the above statement. (d) What is the significance of the negative sign in the energy expression?

3.8 Calculate the following for the ground state of the hydrogen atom: (a) radius of the orbit; (b) velocity of the electron; (c) kinetic energy of the electron; (d) potential energy of the electron; (e) linear momentum of the electron; (f) angular momentum of the electron; and (g) ionisation potential of the atom.

3.9 (a) What do you understand by a monochromatic light source? (b) The spectrum of light emitted from atomic hydrogen is discrete and not continuous—comment on this statement.

3.10 (a) Calculate the wavelength of the line emitted when an electron falls from $n=3$ to $n=2$ in the hydrogen atom. Express the result in wave numbers. (b) Calculate the frequency of the line emitted when an electron falls from $n=6$ to $n=2$ level in the hydrogen atom. What is the approximate ' colour ' of this light?

3.11 (a) State the de Broglie relation between the wavelength and momentum of a particle. (b) Calculate the momentum of a particle which has a de Broglie wavelength of 1A. (c) Estimate the de Broglie wavelength for a cricket ball in flight. (d) Calculate the de Broglie wavelength for:

  (i) a typical hydrogen atom when the gas is at room temperature and

  (ii) an electron which has been accelerated from rest through a potential difference of 150 V

3.12 Compare and contrast the (a) Greek, (b) Dalton, (c) Thomson (d) Rutherford, (e) Bohr, and (f) Schrödinger models of the hydrogen atom.

3.13 Explain the following terms: (a) orbital, (b) quantum numbers, and (c) probability distribution.

3.14 Consider a proton at the origin of the coordinate system and an electron at distance r. (a) Calculate their mutual potential energy. (b) State the various quantum numbers needed to specify the electron behaviour. (c) Mention some observable properties of the system to which these quantum numbers would be related. (d) What range of values can n, l and m_l have? (e) What values do they have for the most stable state of this system?

3.15 What is the ratio of the electrostatic to the gravitational force for an electron and a proton separated from each other by a distance equivalent to the radius of the first Bohr orbit?

3.16 For a one-electron atom with a nuclear charge, $+Ze$, show that Bohr's theory yields energy levels given by $E_n = -\dfrac{2\pi^2 Z^2 m e^4}{n^2 h^2}$

Use this expresion to determine the energy levels of He⁺. Find a line in (*i*) the He⁺ spectrum and (*ii*) the Li²⁺ spectrum which has the same wavelength as the line corresponding to the $n=2 \rightarrow n=1$ transition in the hydrogen atom spectrum.

3.17 It can be shown that the (small) effect of the nuclear motion can be taken into account in the Bohr theory by rewriting the energy expression as $E_n = -2\pi^2 \mu e^4 / n^2 h^2$ where μ called the reduced mass is given by $\mu = mM/m + M$, m being the mass of the electron and M the mass of the nucleus.

Using the above energy expression, calculate the *difference* in the wavelengths corresponding to $n=3 \rightarrow n=2$ transition in a hydrogen atom and a deuterium atom. (It is interesting to note that deuterium was first detected through the small difference in its spectra compared to that of the hydrogen atom.)

3.18 Apply Bohr's theory to a system comprising of a stationary neutron (mass M) and an electron (mass m) revolving around the neutron at a distance r. The attractive force between the neutron and the electron is given by $F = G\,\dfrac{Mm}{r^2}$ where G is the gravitational constant. Write down the expressions for (*i*) the centripetal force, (*ii*) the kinetic energy and the potential energy, and (*iii*) the orbit radii. What is the numerical value of the first Bohr orbit?

3.19 (*a*) What values are assigned to quantum numbers n, l and m_l for: (*i*) a 2*s* orbital; (*ii*) a 2*p* orbital; and (*iii*) a 4*d* orbital. (*b*) What designation is given to an orbital having: (*i*) $n=2$, $l=1$; (*ii*) $n=2$, $l=0$; (*iii*) $n=4$, $l=3$; (*iv*) $n=4$, $l=2$; and (*v*) $n=4$, $l=1$.

3.20 (*a*) Which of the two orbitals, 3*p* or a 4*s* orbital of hydrogen, has the greater energy? (*b*) To remove an electron from the 1*s* orbital of hydrogen, the energy required is the ionisation potential, I. Give the energy required, as a fraction of I, to (*i*) remove an electron from a 3*d* orbital and (*ii*) promote an electron from the 1*s* to the 3*d* orbital? (*c*) In any atom other than hydrogen, 2*p* orbital has a higher energy than 2*s* orbital. Comment on this statement. (*d*) Place the following orbitals in order of increasing energies: 3*d*, 4*s* and 4*p*.

3.21 Name the quantum numbers which are related to the angular momentum of the electron, and give the quantum number which characterises the shape of an orbital.

3.22 For an atom placed in a magnetic field, how many different values of angular momentum along the field direction can be assumed by (*a*) an *s* electron; (*b*) a *p* electron; and (*c*) an electron with orbital quantum number l?

3.23 (*a*) How many quantum numbers are required to designate (*i*) the space part of an electron wave function and (*ii*) the complete wave function. (*b*) Give the maximum number of electrons that can occupy the 3*d* sub-shell. (*c*) What is the total number of electrons that can occupy an orbital with $n=3$?

3.24 (*a*) Write the ground state electron configuration of (*i*) C($Z=6$) and (*ii*) Ne($Z=10$). (*b*) What do you understand by a closed-shell configuration? Give examples. (*c*) What is a half-filled shell electron configuration? Give two examples. (*d*) Which of the species —H, He, Li, Li⁺, Be, Be⁺²—has a closed-shell configuration?

3.25 In each of the following pairs, pick out the orbital in which the electron is closer to the nucleus

    (*a*) 1*s* and 2*s*; (*b*) 2*s* and 2*p*; and (*c*) 4*s* and 4*f*.

Will the answer depend upon whether one is considering a one-electron atom or a multi-electron atom?

3.26 Suppose that energy in a multi-electron atom depends only upon the principal quantum number (i.e. 2*s*=2*p*, 3*s*=3*p*=3*d*, 4*s*=4*p*=4*f*, etc.). Assuming the validity of the Pauli

principle, write the electronic configuration of the elements from $Z=15$ to $Z=30$. What will be the nature of the periodic table?

3.27 Assuming the Pauli principle is not required, write the electronic configuration of the elements from $Z=1$ to $Z=10$. What will be the nature of the periodic table under these conditions?

3.28 Would you expect the $2s$ electron in lithium atom to have the same, greater or less stability than a $2s$ electron in the hydrogen atom? Explain.

3.29 Account for the observation that negative ions are generally larger than the positive ions, if the ions are isoelectronic.

3.30 Discuss the trends in ionisation energy of elements within a family. Of the two factors, nuclear charge and the radius, which has a more significant effect?

3.31 For each of the following pairs, state which one has the greater ionisation energy and greater electron affinity: (a) I, I$^-$; (b) Br, K; (c) S, Te; (d) Sr, Ra; (e) Li, Li$^+$; and (f) Br, I.

3.32 The first three ionisation energies of the boron atom are: 8·3 eV; 25·1 eV; 37·9 eV; and 259·3 eV. Explain the magnitudes in terms of the electron configuration of boron and deduce the number of valence electrons of boron.

3.33 Which of the following electron configurations would you expect to have the lowest ionisation energy? Explain.

(a) $1s^2 2s^2 2p^6$; (b) $1s^2 2s^2 2p^5$; **and** (c) $1s^2 2s^2 2p^6 3s^1$.

3.34 Explain why the electron affinity of the atoms increases from left to right along a row in the periodic table.

3.35 Calculate the number of unpaired electrons in (a) Zn, Zn$^+$, Zn^{2+}, Zn^{3+} and (b) Ni, Ni$^+$, Ni^{2+}, Ni^{3+}. Assume that the $4s$ electron is removed before the $3d$ electron.

4

Chemical Bonding and
Molecular Structure

The theory of the chemical bond...is still far from perfect. Most of the principles that have been developed are crude, and only rarely can they be used in making an accurate quantitative prediction. However, they are the best that we have, as yet, and I agree with Poincaré that 'it is far better to foresee even without certainty than not to foresee at all '.

LINUS PAULING

We discussed the electronic structure of atoms in Chapter 3 and indicated the correlation between atomic properties and electronic structure. An understanding of atomic properties, however, contributes only in a small way towards the interpretation of the behaviour of matter since except for noble gases, no other elements or compounds exist as atoms under ordinary conditions. In all other cases, atoms are present as aggregates which have properties quite different from those of the individual atoms comprising them. Atomic aggregates occur as molecules, as macromolecules, or as giant networks. While the first two types are found in all the three states of aggregation, the last type exists only in the solid state. As shown in Chapter 2, we can deduce from chemical evidence that atoms combine to form larger units and the stability of these units is due to chemical bonds. The structureless atom of Dalton could neither account for the properties of these aggregates nor explain the nature of the chemical bond. We shall now examine how the modern atomic theory tackles these problems. Our primary concern in this chapter is with molecules; macromolecules and solid state networks are mentioned only in passing. A fuller discussion of them is given in Chapters 7 and 18.

4.1 GENERAL CHARACTERISTICS OF MOLECULES

There are several features which are common to all molecules. Some of the more important ones are: (a) Only a definite, and not an arbitrary, number of atoms are present in a molecule. Thus, hydrogen molecule is H_2, methane is CH_4, sucrose is $C_{12}H_{22}O_{11}$ and so on; stable molecular species corresponding

to say, H_3, CH_5 or $C_{12}H_{22}O_{12}$ are not known. (b) Molecules exhibit definite geometry and shapes. For example, CO_2 is linear, H_2O is angular, CCl_4 is tetrahedral and C_6H_6 is a hexagonal ring. The ordering of atoms in a molecule is also definite. Thus, CO_2 is OCO, N_2O is NNO. Any other geometries or any other ordering for these molecules is not known. (c) The distances and the angles in a molecule are fixed.* For example, the H—H bond distance in H_2 molecule is 0·74 A and the HOH angle in H_2O molecule is about 104°. (d) Energy is required to break (dissociate) a molecule. In other words, energy is lowered when a group of atoms form a molecule. For example, 104 kcal are needed to dissociate one mole of molecular hydrogen which means that when isolated hydrogen atoms combine to form one mole of hydrogen molecules, 104 kcal of energy is released.

All the features listed above arise from a single principle—the principle of minimum energy. The number of atoms in a molecule, their ordering, their relative spacing and the overall molecular shape are all fixed because the energy of the molecule is minimum (relative to isolated atoms) only for a particular number and arrangement of the constituent atoms. The classical concept of a chemical bond (Chapter 2) is just a symbolic way to denote this energy lowering. The great merit of the 'electronic' atom is that, by providing an insight into the different mechanisms of energy lowering in terms of electron behaviour it yields an understanding of the nature and types of chemical bonding and of molecular structure.

4.2 THE COVALENT BOND

Most chemists regard the covalent bond as *the* chemical bond not only because of its widespread occurrence but also because an understanding of the covalent bond provides the background for understanding other types of bonding. Even though the covalent bond in a vast majority of molecules involves sharing of an electron pair, we begin by examining the covalent bond in H_2^+ since the nature of this bond is most clearly revealed in this simple example.

4.2.1 Hydrogen Molecule Ion (H_2^+)—the Simplest Molecule

The hydrogen molecule ion (H_2^+) is the only molecular system for which the exact wave function can be obtained by solving the Schrödinger equation. Though H_2^+ is not particularly important chemically, its significance lies in the fact that being the simplest molecule, it provides a basis for discussion of chemical bonding and molecular structure in the same way that hydrogen atom (the simplest atom) does for atomic structure.

H_2^+ is not stable enough to be prepared under ordinary conditions and it is produced in discharge tubes only. Although H_2^+ is short-lived, it exists long enough to permit measurement of its properties. It is found that the bond length in H_2^+ is 1·06 A, the dissociation energy is 64 kcal/mol and the molecule is paramagnetic. The spectrum of the molecule is also known. All the properties of H_2^+ can be calculated exactly and they are in perfect agreement with experiment thus showing that quantum mechanics can satisfactorily account for molecule formation.

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*This statement does not mean that the atoms in a molecule are rigidly held. During vibrations and rotations of a molecule, the relative positions of the atoms change. The values for distances and angles usually quoted are the time-averages and these have fixed values.

4.2.2 Exact Description of H_2^+

The exact quantum description of H_2^+ shows that the lone electron can have a large number of permitted states, a wave function being associated with each state. The square of the wave function gives the probability distribution of the electron in the appropriate state. In each state, energy has a sharp value, but the position does not. Moreover, energy changes discontinuously from one state to another (i.e. energy is quantised).* The lowest energy state is called

Fig. 4.1 The variation of energy of H_2^+ as a function of internuclear distance. The minimum in energy occurs when the distance is 1.06 A which is the bond length. The energy at this distance is lower by 64 kcal/mol compared to the energy at infinite separation. 64 kcal/mol is therefore the dissociation energy or the bond energy of the molecular ion. For distances smaller than the bond length, the energy increases because of the nuclear repulsion.
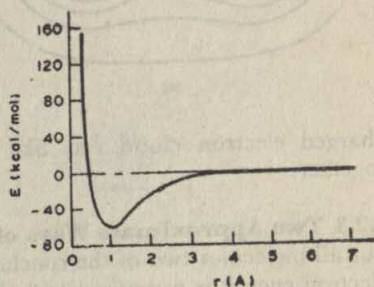
the ground state. All these results are analogous to the ones obtained in the hydrogen atom case.

The energy of H_2^+ can be theoretically calculated as a function of the inter-nuclear distance and the resulting plot is shown in Fig. 4.1. The energy of the system ($H^+ + H$) for infinite separation of the proton and the hydrogen atom is taken as reference and assigned the zero value. As the separation reduces from infinite distance, the energy is lowered until a minimum value is reached, the energy then increases as the distance is reduced further. The configuration of a molecule for which the energy is minimum corresponds to the normal state of the molecule. This statement is true in all cases, but in polyatomic molecules the energy depends on several interatomic distances and angles, and the simultaneous variation of energy as a function of all these variables is difficult to show graphically. In H_2^+, the minimum occurs when the internuclear separation is 1·06 A which, therefore, is the bond length in the molecule. The energy at this point is -64 kcal/mol, which therefore is the negative of the dissociation energy of the molecule. Both these numbers agree with the experimental values quoted earlier.

It is instructive to examine the probability distribution of the electron in the ground state of H_2^+ (Fig. 4.2). The reason for energy lowering in molecule formation is revealed if we compare this with the probability distribution in the ground state of two non-bonded hydrogen atoms (Fig. 4.3). We see that the electron probability between the nuclei in the molecule has increased at the expense of the probability outside the nuclei. The region between the nuclei is energetically favourable since the electron here can simultaneously feel the attraction due to both the nuclei. The increased probability in this region in the molecule accounts for the lowering of energy, or in other words, accounts for the stability of the molecule. It is as if the concentration of the negatively

*No general statement about electron angular momentum can be made for molecules. Only in linear molecules, the component of angular momentum along the bond axis is sharp.
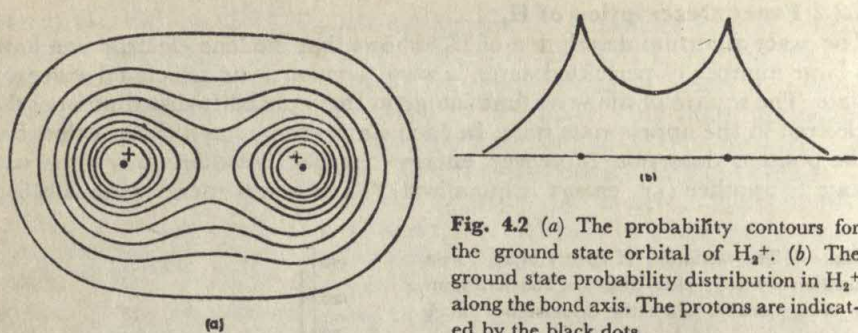
Fig. 4.2 (*a*) The probability contours for the ground state orbital of H_2^+. (*b*) The ground state probability distribution in H_2^+ along the bond axis. The protons are indicated by the black dots.

charged electron cloud acts like electrostatic cement holding the nuclei together.

4.2.3 Two Approximate Ways of Looking at the Exact Description

For all molecules two of the conclusions reached above remain valid: (*a*) the electron energy is quantised and (*b*) molecule formation takes place because the electron (or electrons) can simultaneously feel attraction due to more than one nucleus. The discussion of complex molecules cannot, however, be carried out in terms of exact wave functions and one has to resort to approximations. The same difficulty was encountered in multi-electron atoms where approximate atomic orbitals were constructed in analogy to the exact hydrogen atomic orbitals. In multi-electron molecules, there are two possible approximate descriptions. These are known as the *molecular orbital* (MO) method and the *valence*

Fig. 4.3 The broken line shows the electron probability distribution for two non-bonded protons. The solid line shows the probability distribution if the two protons are bonded as in H_2^+. The increase in probability in the internuclear region is the prime cause of bonding.
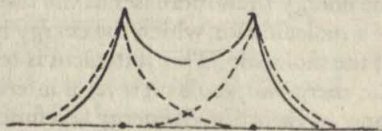
bond (VB) method. It should be realised that we have more than one method for describing the structure of molecules because we are forced to look for approximate behaviour. Had our treatment been exact, there would have been only one answer. The MO theory as well as the VB theory have advantages and disadvantages; as the two methods are refined further, they approach each other. Let us now discuss how the exact description of the H_2^+ ion suggests the MO and the VB approaches.

4.2.4 Molecular Orbital Approach

In the MO approach, the behaviour of each electron in a multi-electron molecule is described by a one-electron wave function. In analogy with the atomic case, these molecular wave functions are called molecular orbitals. The question confronting the MO theory is, how to construct these approximate molecular orbitals? The exact probability distribution of H_2^+ suggests an answer. In the MO language, one could say that the exact distribution has been obtained from the exact MO for H_2^+. However, a reasonable approximation to the exact distribution can be constructed by adding two $1s$ atomic orbitals centered

(a)

(b)

(c)

Two s atomic orbitals   Molecular orbital

(d)
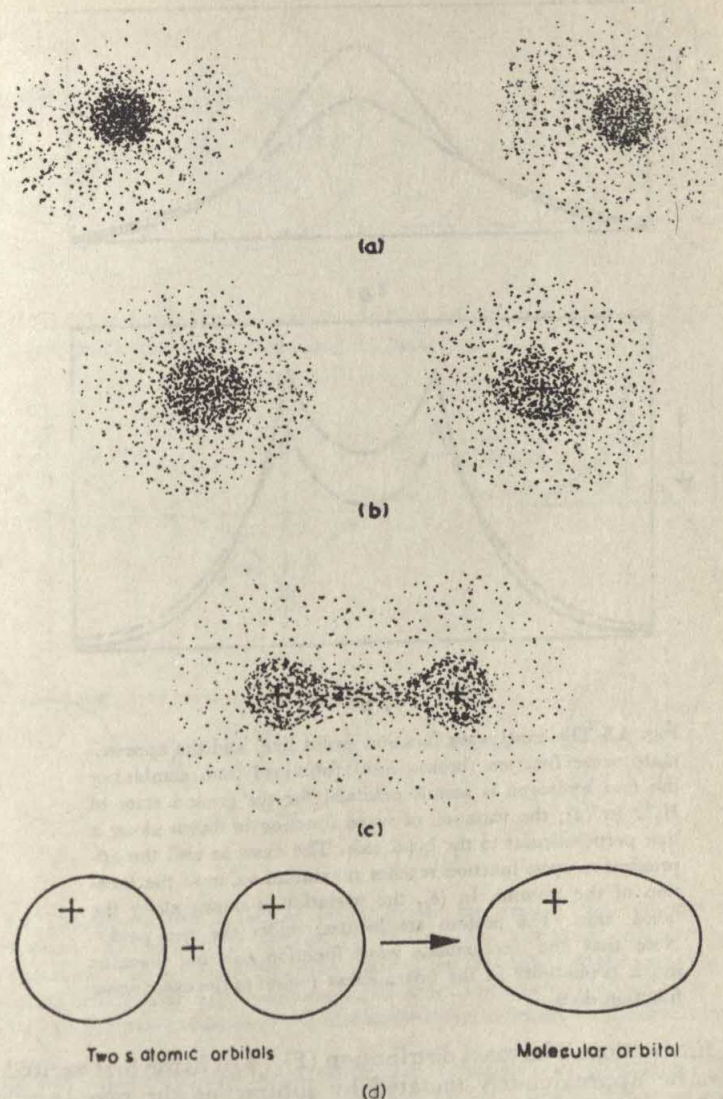
Fig. 4.4 The formation of the ground state molecular orbital of H_2^+ from the two $1s$ atomic orbitals of the hydrogen atom. (*a*) The atomic orbitals are shown when the nuclei are far away. (*b*) The atomic orbitals begin to distort as the nuclei approach each other close enough for significant interaction. (*c*) The atomic orbitals have lost their identity in the resulting molecular orbital. (*d*) The boundary surface representation of the molecular orbital and the component atomic orbitals.

on the two hydrogen nuclei. Fig. 4.4 shows some ways of picturing the interaction between two $1s$ atomic orbitals to form a molecular orbital. The approximate MO does not place as much probability in the internuclear region as the exact MO (see Fig. 4.5), but it roughly reproduces the characteristics of

(a)

(b)
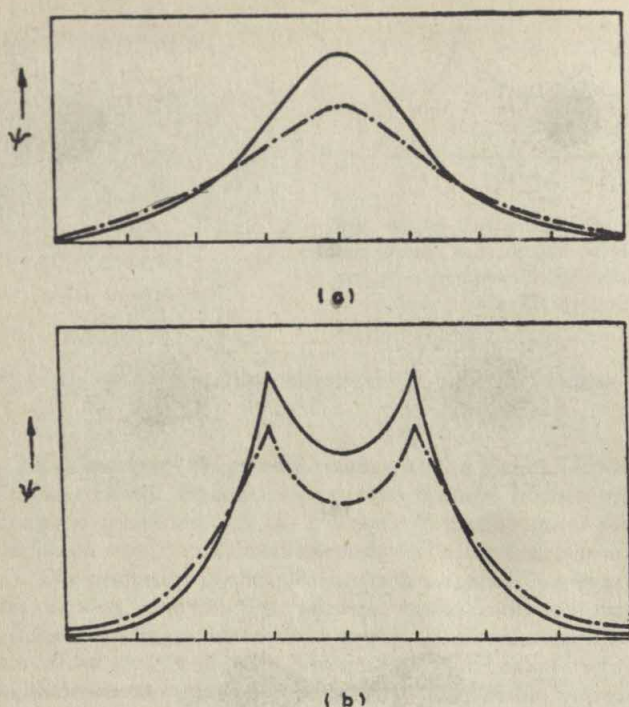
Fig. 4.5 The exact wave function (solid line) and the approximate wave function (broken line) (obtained from combining the two hydrogen $1s$ atomic orbitals) for the ground state of H_2^+. In (a), the variation of wave function is shown along a line perpendicular to the bond axis. The exact as well the approximate wave function reaches maximum value at the location of the protons. In (b), the variation is shown along the bond axis. The protons are located under the two peaks. Note that the approximate wave function does not place as much probability in the internuclear region as the exact wave function does.

the exact distribution. The exact distribution (Fig. 4.6) in the first excited state of H_2^+ can be approximately imitated by subtracting the two $1s$ orbitals. In Fig. 4.7, we have shown the subtraction of the radial and angular parts centered on the two hydrogen nuclei. The MO theory generalises this conclusion by stating that approximate molecular orbitals can be generated by adding and subtracting suitable atomic orbitals. If the resulting MO increases the electron probability between the nuclei (compared to nonbonded atoms), it favours bonding and is, therefore, called a *bonding molecular orbital*. If it decreases the probability, it discourages bonding and is therefore called an *anti-bonding molecular orbital.**

*This feature can be explained algebraically. Let ϕ_a and ϕ_b be the two atomic orbitals centered on the two nuclei. Then the bonding molecular orbital (say ϕ_1) will be given by $\phi_a + \phi_b$ while the antibonding MO (say ϕ_2) will be given by $\phi_a - \phi_b$. Squaring the functions we have,
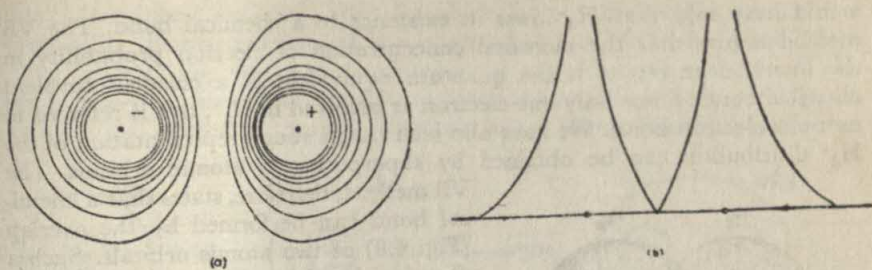
Fig. 4.6 (*a*) The probability contours for the first excited state orbital of H_2^+.(*b*) The first excited state probability distribution along the bond axis.
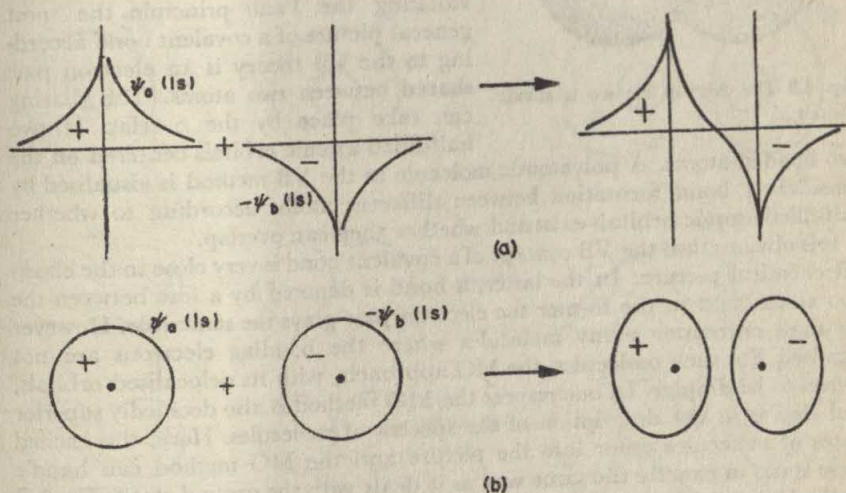
Fig. 4.7 The approximate molecular orbital for the first excited state obtained by subtracting the two 1s hydrogen atomic orbitals. (*a*) The radial part of the atomic and the molecular wave functions. The square of the radial part of the molecular orbital gives the probability distribution which is an approximation to the exact distribution shown in Fig. 4.6(*b*). The boundary surface representation of the first excited state molecular orbital is shown in (*b*).

The MO approach can be summarised as follows: (*a*) construct approximate molecular orbitals from atomic orbitals, (*b*) arrange them in a sequence of increasing energy and (*c*) place electrons in the MOs subject to the Pauli principle and electron repulsion consideration. The electronic configuration of molecules can then be written and the relation of the configuration to molecular properties can be established in the same manner as was done for atoms.

4.2.5 Valence Bond Approach
We have seen that H_2^+ is stable compared to the isolated atoms because the electron has more probability to be between the two nuclei. Classically, we

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$\psi_1{}^2 = \psi^2{}_a + \psi^2{}_b + 2\psi_a\psi_b$ and $\psi^2{}_2 = \psi^2{}_a + \psi^2{}_b - 2\psi_a\psi_b$. It is obvious from this that the term $2\psi_a\psi_b$ contributes to the probability distribution in the $\psi^2{}_1$ (bonding orbital) while it subtracts in $\psi^2{}_2$ (anti-bonding).

would have said that H_2^+ owes its existence to a chemical bond. The VB method argues that the increased concentration of electron probability in the internuclear region is the quantum equivalent of a classical covalent chemical bond. Since only one electron is involved in H_2^+, this is referred to as a one-electron bond. We have also seen that a rough representation of the H_2^+ distribution can be obtained by superposing 1s atomic orbitals. The VB method, therefore, states that a chemical bond can be formed by the overlap (Fig. 4.8) of two atomic orbitals. Such a chemical bond is called a covalent bond. Since two electrons with opposite spin can be placed between two nuclei without violating the Pauli principle the most general picture of a covalent bond according to the VB theory is an electron pair shared between two atoms. The sharing can take place by the overlap of two half-filled atomic orbitals centered on the two bonded atoms. A polyatomic molecule in the VB method is visualised by considering bond formation between different atoms according to whether half-filled atomic orbitals exist and whether they can overlap.

Fig. 4.8 The overlap of two 1s atomic orbitals

It is obvious that the VB concept of a covalent bond is very close to the classical chemical picture. In the latter, a bond is denoted by a line between the two atoms, and in the former the electron pair plays the same role. However we shall encounter many molecules where the bonding electrons are not localised. For such molecules, the MO approach, with its delocalised orbitals, proves to be simpler. In one respect the MO method is also decidedly superior and that is in the description of the spectra of molecules. Here, the excited states of molecules enter into the picture and the MO method can handle these states in exactly the same way as it deals with the ground state. The VB method is unwieldy and cumbersome in this regard. We shall now illustrate the use of both the MO and VB approaches by discussing several examples.

4.3 DIATOMIC MOLECULES—ILLUSTRATION OF THE MOLECULAR ORBITAL METHOD

The simplicity and usefulness of the MO approach can be easily appreciated by considering the electronic structure of some homonuclear diatomic molecules. The procedure followed in this case is similar to the *aufbau* principle adopted for discussing the structure of multi-electron atoms (Chapter 3). There, we arranged the various atomic orbitals in the order of increasing energy and then fed the electrons into the orbitals. Similarly, for homonuclear diatomics the various approximate molecular orbitals are placed in a sequence of increasing energy and the electrons are then alloted to these orbitals. In this instance also, electron assignment is subject to the Pauli principle.

4.3.1 Labelling of Molecular Orbitals

In analogy with the s, p, d designation of atomic orbitals, molecular orbitals are named as σ, π, δ, etc. The significance of this designation is as follows. The addition or subtraction of two s atomic orbitals centered on two

nuclei produces resultant orbitals which have cylindrically symmetrical probability distribution around the internuclear axis. Such MOs are of the *sigma* (σ) *type* (Fig. 4.9). The combination of *p* type atomic orbitals can also produce σ-type molecular orbitals. If internuclear axis is defined as *Z*-axis, both the MOs obtained from p_z orbitals would have cylindrical symmetry;
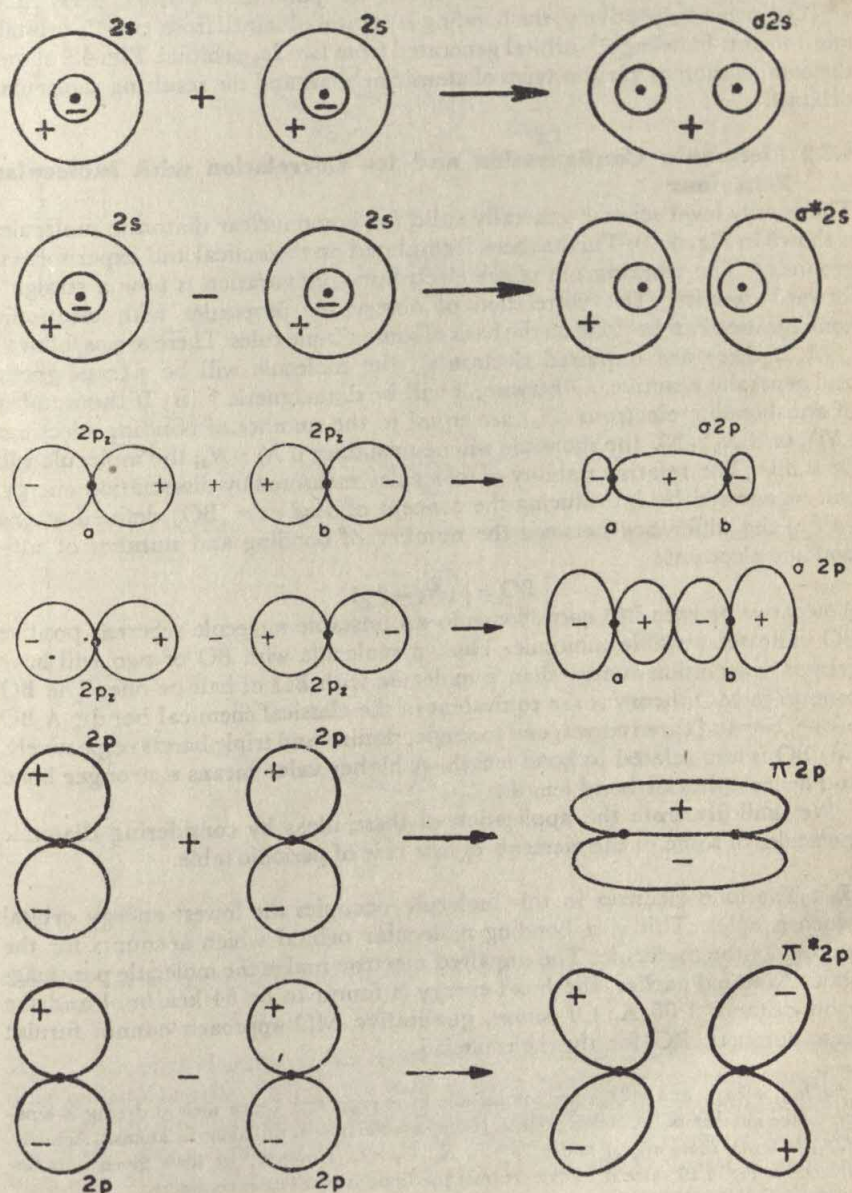
Fig. 4.9 The formation of various excited state molecular orbitals from the hydrogen atom atomic orbitals. The molecular orbital designations (σ1s, π_{2p}^*, etc.) are explained in the text.

the combinations of p_y or of p_x orbitals would not have cylindrical symmetry. They would have instead a nodal plane containing the internuclear axis. Such MOs are designated as *pi* (π) *orbitals* (Fig. 4.9). The anti-bonding orbitals are indicated by putting an asterisk. Thus, σ^* and π^* orbitals are *anti-bonding σ- and π-orbitals* respectively. Atomic orbitals which are involved in the formation of molecular orbitals are given in parenthesis; thus, $\sigma(2s)$ and π^* $(2p_y)$ mean respectively, the bonding σ orbital obtained from two $2s$-orbitals and the anti-bonding π^* orbital generated from two $2p_y$-orbitals. Fig. 4.9 shows the combination of various types of atomic orbitals and the resulting molecular orbitals.

4.3.2 Electronic Configuration and its Correlation with Molecular Behaviour

The energy level scheme generally valid for homonuclear diatomic molecules is shown in Fig. 4.10. This has been formulated on theoretical and experimental grounds.* The working out of the electronic configuration is now a straightforward exercise. The correlation of observable properties with electronic configuration can be done on the basis of some simple rules. These are as follows:

(*i*) If there are unpaired electron(s), the molecule will be paramagnetic and generally reactive. Otherwise, it will be diamagnetic.† (*ii*) If the number of anti-bonding electrons (N_a) are equal to the number of bonding electrons (N_b), or if $N_a > N_b$, the molecule will be unstable; if $N_b > N_a$, the molecule will be stable. The relative stability of molecules measured by dissociation energy, can be assessed by introducing the concept of *bond order* (BO) defined as one half of the difference between the number of bonding and number of anti-bonding electrons:

$$BO = \tfrac{1}{2} (N_b - N_a)$$

A negative or zero BO corresponds to an unstable molecule whereas positive BO indicates a stable molecule. Thus, a molecule with BO of two will have greater dissociation energy than a molecule with BO of half or one. The BO concept in MO theory is the equivalent of the classical chemical bond.‡ A BO of one, two and three correspond to single, double and triple bonds respectively. (*iii*) BO is also related to bond length. A higher value means a stronger bond and hence a shorter bond length.

We shall illustrate the application of these ideas by considering diatomic molecules of some of the elements of first row of periodic table.

H_2^+: The lone electron in this molecule occupies the lowest energy orbital which is $\sigma(1s)$. This is a bonding molecular orbital which accounts for the stability of the molecule. The unpaired electron makes the molecule paramagnetic. As stated earlier, the bond energy is found to be 64 kcal/mol and the bond distance 1·06 A. Of course, qualitative MO approach cannot furnish these numbers. BO for the molecule is $\tfrac{1}{2}$.

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*$\sigma(2p_z)$, $\pi(2p_x)$, and $\pi(2p_y)$ are comparable in energy and hence their ordering is sensitive to the number of electrons present. (Compare the $3d$—$4s$ situations in atoms.) Actually, $\sigma(2p_z)$ is lower than $\pi(2p_x)$ and $\pi(2p_y)$ in N_2, F_2, O_2. However, we have given only one sequence in Fig. 4.10 since it leads to correct predictions in all cases considered.

†The connection between electronic structure and magnetism was discussed in Chapter 3.

‡However, BO is fractional in many examples discussed below. There is no classical analogue of fractional BO.
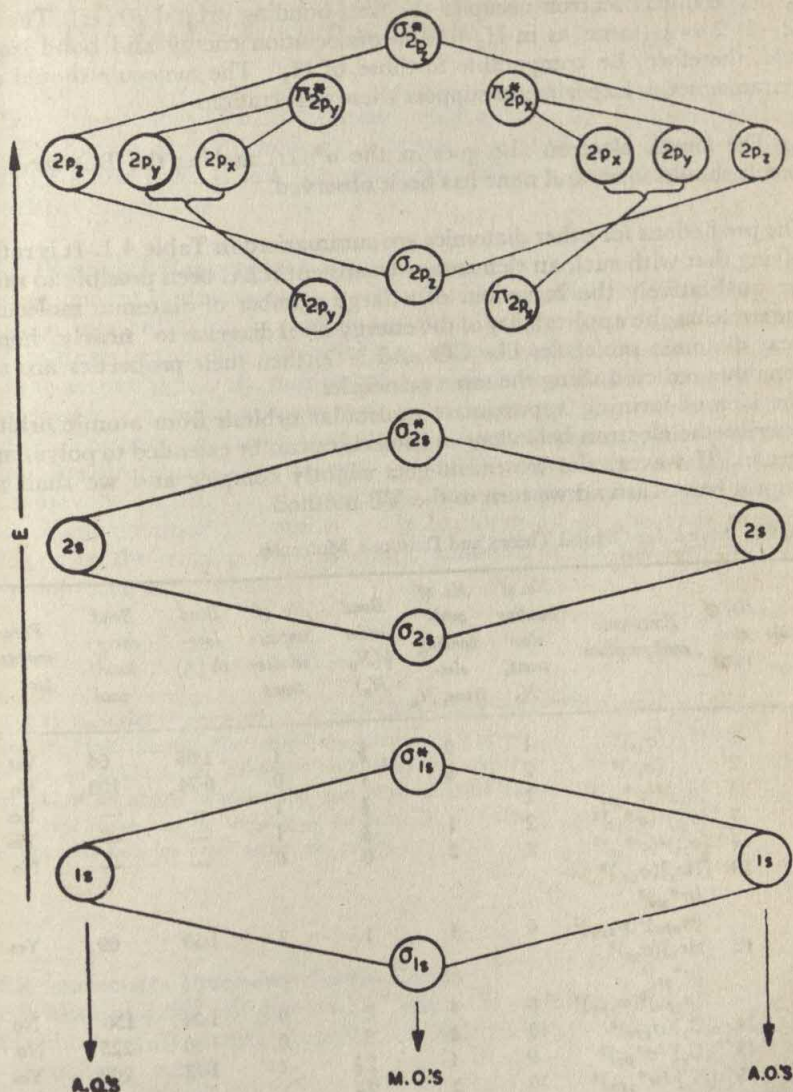
Fig. 4.10 The energy level diagram for the molecular orbitals of the homonuclear diatomic molecules

H_2: The second electron of this two-electron molecule will also go in the bonding molecular orbital $\sigma(1s)$ but with opposite spin. The molecule should be diamagnetic. Because two electrons are present in the bonding orbital as against one in H_2^+, BO will be one and the dissociation energy of H_2 should be greater than that of H_2^+. The dissociation energy of H_2 is 104 kcal/mol, a value less than twice the H_2^+ value, since electron repulsion reduces the stability. The bond in H_2 should be shorter than in H_2^+, in agreement with experiment (experimental value = 0·74 A).

He_2^+: The third electron occupies the anti-bonding orbital $\sigma^*(1s)$. The BO is $(2-1)/2 = \frac{1}{2}$ (same as in H_2^+). The dissociation energy and bond length should, therefore, be comparable to those of H_2^+. The molecule should also be paramagnetic. Experiments support these expectations.

He_2: The fourth electron also goes in the $\sigma^*(1s)$ making the BO zero. No molecule should form and none has been observed.

The predictions for other diatomics are summarised in Table 4.1. It is rather satisfying that with such an elementary treatment it has been possible to rationalise qualitatively the behaviour of a large number of diatomic molecules. If one stretches the applicability of the energy level diagram to 'nearly' homonuclear diatomic molecules like CO and NO, then their properties are also reasonably predicted using the same principles.

The idea of forming approximate molecular orbitals from atomic orbitals to describe the electron behaviour in molecules can be extended to polyatomic molecules. However, the treatment gets slightly complex and we shall not attempt it here. Instead we turn to the VB method.

Table 4.1 Molecular Orbital Theory and Diatomic Molecules

Molecule	No. of electrons	Electronic configuration	No. of bonding electrons, N_b	No. of antibonding electrons, N_a	Bond order $\frac{1}{2}(N_b - N_a)$	No. of unpaired electrons	Bond length (A)	Bond energy kcal/mol	Paramagnetic
H_2^+	1	$(\sigma_{1s})^1$	1	0	$\frac{1}{2}$	1	1·06	64	Yes
H_2	2	$(\sigma_{1s})^2$	2	0	1	0	0·74	103	No
H_2^-	3	$(\sigma_{1s})^2(\sigma^*_{1s})^1$	2	1	$\frac{1}{2}$	1	—	—	Yes
He_2^+	3	$(\sigma_{1s})^2(\sigma^*_{1s})^1$	2	1	$\frac{1}{2}$	1	—	—	Yes
He_2	4	$(\sigma_{1s})^2(\sigma^*_{1s})^2$	2	2	0	0	—	—	No
B_2	10	$[He_2](\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2px})^1(\pi_{2py})^1$	6	4	1	2	1·59	69	Yes
C_2	12	$[He_2](\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2px})^2(\pi_{2py})^2$	8	4	2	0	1·24	150	No
N_2	14	$[C_2](\sigma_{2pz})^2$	10	4	3	0	1·10	225	No
N_2^+	13	$[C_2](\sigma^2_{pz})^1$	9	4	$2\frac{1}{2}$	1	1·12	200	Yes
N_2^-	15	$[N_2](\pi^*_{2px})^1$	10	5	$2\frac{1}{2}$	1	—	—	Yes
O_2	16	$[N_2](\pi^*_{2px})^1(\pi^*_{2py})^1$	10	6	2	2	1·21	118	Yes
O_2^+	15	$[N_2](\pi^*_{2px})^1$	10	5	$2\frac{1}{2}$	1	1·12	149	Yes
O_2^-	17	$[N_2](\pi^*_{2px})^2(\pi^*_{2py})^1$	10	7	$1\frac{1}{2}$	1	1·28	—	Yes
F_2	18	$[N_2](\pi^*_{2px})^2(\pi^*_{2py})^2$	10	8	1	0	1·44	36	No
Ne_2	20	$[F_2](\sigma^*_{2pz})^2$	10	10	0	0	—	—	No
CO	14	$[C_2](\sigma_{2pz})^2$	10	4	3	0	1·13	256	No
NO	15	$[N_2](\pi^*_{2px})^1$	10	5	$2\frac{1}{2}$	1	1·15	162	Yes

4.4 DIATOMIC AND POLYATOMIC MOLECULES—ILLUSTRATION OF THE VALENCE BOND METHOD

The essence of the VB approach is that the overlap of half-filled orbitals centered on two atoms leads to bond formation between them. The covalent bond involves the sharing of an electron pair with opposite spins. The larger the overlap stronger is the bond. These two principles suffice to describe the structure of a variety of molecules.

4.4.1 Pictorial Representation

It is convenient to represent the overlap of orbitals pictorially. Thus, the overlap between two half-filled $1s$ orbitals on the two hydrogen atoms in hydrogen molecule can be shown as in Fig. 4.11(a), where the circles represent the orbitals and the arrows signify the number of electrons in it and their spin orientation. The dotted box indicates overlap of the orbitals and the resulting bond formation. This may be termed as the orbital representation. A still simpler way is to indicate electrons by dots. H_2 molecule can then be shown as in Fig. 4.11 (b). This may be called the electron dot representation or Lewis* structures. This scheme naturally contains no information about the type of orbitals involved in the overlap. In either representation, it is customary to indicate only the valence electrons.

Fig. 4.11 Pictorial representations of the valence bond view of the H_2 molecule. (a) The orbital representation. The circles denote orbitals, the arrows denote electrons and the direction of an arrow indicates the spin of an electron. The dotted box represents the overlap of orbitals. (b) The electron dot structure (or Lewis structure) of H_2.
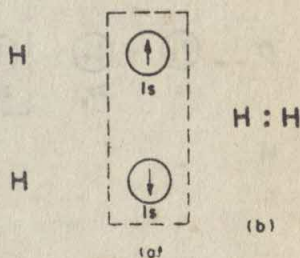
4.4.2 Molecules Involving Single Bonds

Some examples are now given which show the usefulness of the valence bond method. We first restrict ourselves to molecules involving a 'single bond' in the classical sense.

F_2: The ground state configuration of the fluorine atom is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$. In the orbital as well as the electron dot representations, only the valence electrons, namely $2s^2 2p_x^2 2p_y^2 2p_z^1$, are shown (Fig. 4.12a). The $2p_z$ orbital of one fluorine atom with one unpaired electron, say with spin up, can overlap with the $2p_z$ orbital of another fluorine atom with spin down, to form an electron pair which is shared by the two fluorines, resulting in the molecule formation. We thus expect F_2 to be non-magnetic and to have a single bond as is observed.

*G. N. Lewis, one of the outstanding chemists of this century, was the first one in 1916, to put forward an 'electronic' interpretation of the chemical bond.

(a)

(b)

(c)

He (↕)
   ls

No bond possible

He (↕)
   ls

(d)
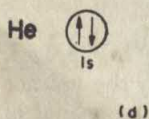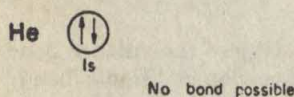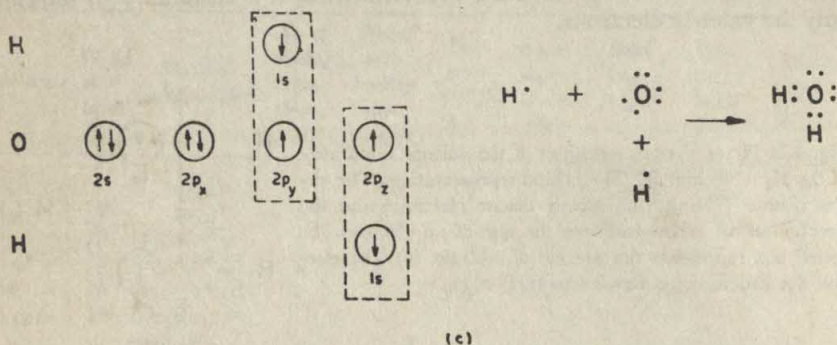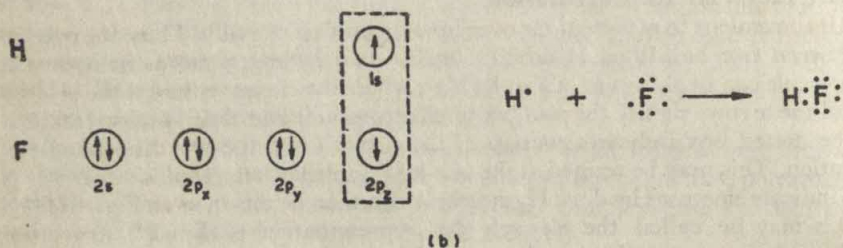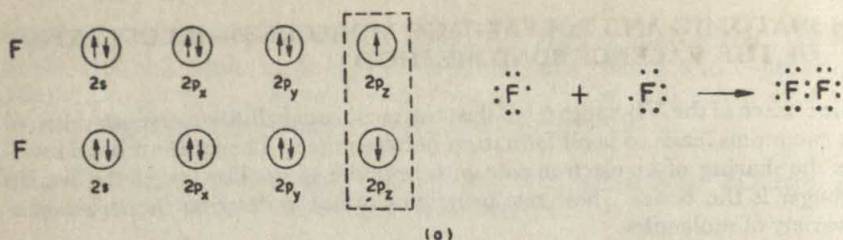
Fig. 4.12 The orbital and the electron dot representations of various molecules. Only the valence electrons are shown in each case.

HF: The $2p_z$ orbital of fluorine atom can overlap with $1s$ orbital of a hydrogen atom (containing an unpaired electron of opposite spin) to form HF molecule (see Fig. 4.12*b*).*

*The electron-pair in this molecule and some other molecules is not equally shared. This point is discussed further in section 4.5.
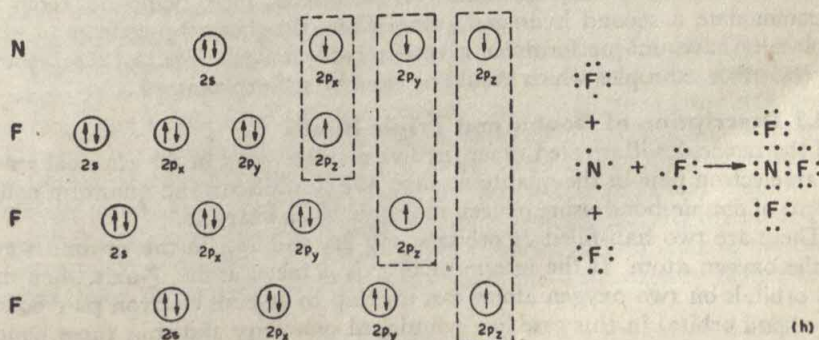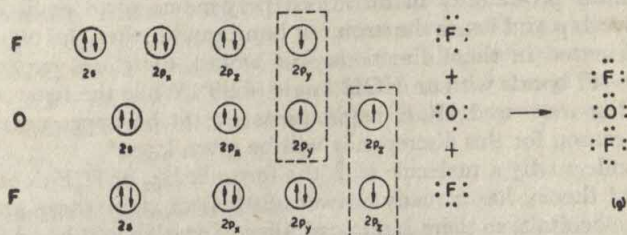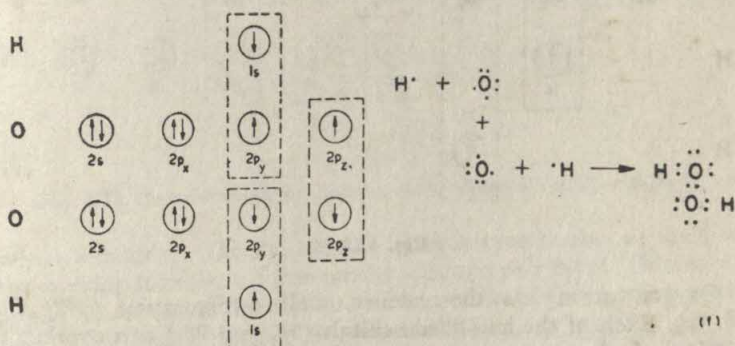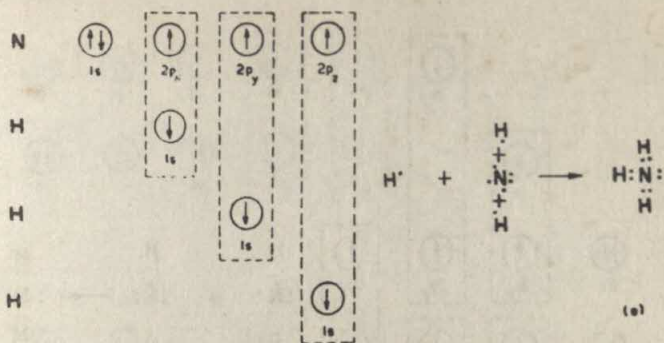
Figs. 4.12 (e–h)
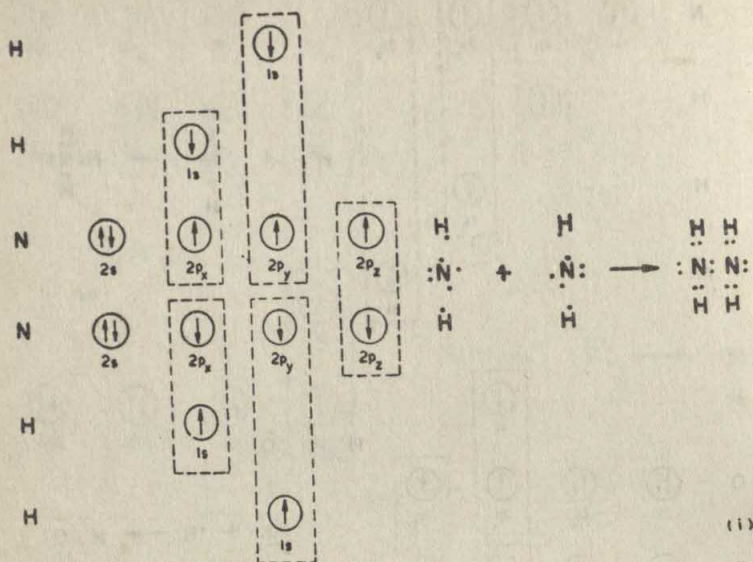
Fig. 4.12 (i)

H_2O: Oxygen atom has the valence shell configuration $2s^2 2p_x^2 2p_y^1 2p_z^1$ (Fig. 4.12c). Each of the half-filled orbitals ($2p_y$ and $2p_z$) can overlap with a $1s$ orbital of a hydrogen atom to form a single O—H bond. Since $2p_y$ and $2p_z$ have maximum probability in directions perpendicular to each other, the maximum overlap and hence the strongest bond results when the two hydrogen atoms are situated in these directions. We would, therefore, expect H_2O to have two O—H bonds with an HOH angle of 90°. While the first expectation is verified, the measured HOH angle turns out to be approximately 105°. A plausible reason for this discrepancy will be given later.*

If one wonders why a molecule with the formula He_2 or H_2F does not exist, valence bond theory has a ready answer. In helium atom, there are no half-filled valence orbitals, so there is no possibility of overlap and bond formation. The situation is depicted in Fig. 4.12(d). In fluorine atom, there is only one half-filled orbital, so only one bond can be formed, there being no room to accommodate a second hydrogen atom. Thus the classical puzzle as to why molecules have unique formulae is rather easily solved. Figs. 4.12(e–i) show several other examples which should by now be self-explanatory.

4.4.3 Description of Double and Triple Bonds

All the molecules illustrated so far involve a single bond in the classical sense or an electron pair in the quantum sense. We now discuss the quantum equivalent of double bond using oxygen molecule as an example.

There are two half-filled $2p$ orbitals, say $2p_y$ and $2p_z$, in the ground state of the oxygen atom. If the internuclear axis is taken as the Z-axis, then the $2p_z$ orbitals on two oxygen atoms can overlap to give an electron pair bond. The bond orbital in this case has cylindrical symmetry and thus these bonds

*The shapes and geometries of molecules are considered in detail in section 4.6.

(a)

(b)
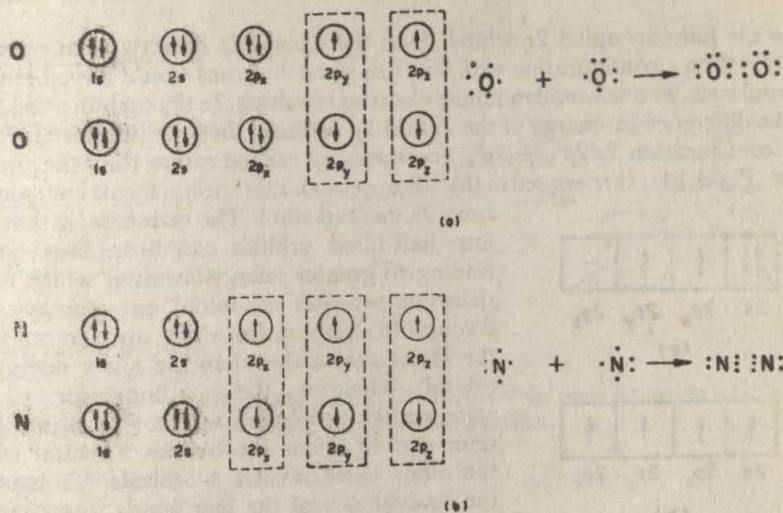
Fig. 4.13 The orbital and the electron dot structures of (a) O_2 and (b) N_2

are called σ bonds.* The $2p_y$ orbitals lying perpendicular to the bond axis can also overlap laterally to form another electron pair bond. This bond orbital has a nodal plane and so the bond is called a π bond. The quantum version of a double bond thus consists of two electron pairs, one electron pair forming the σ bond and the other forming the π bond. N_2 molecule is a straight-forward extension. Nitrogen atom has three half-filled $2p$ orbitals namely $2p_x$, $2p_y$ and $2p_z$. The $2p_z$ orbital overlap between two nitrogen atoms gives the σ bond whereas lateral overlap between the two $2p_x$ and the two $2p_y$ gives two π bonds. One σ and two π bonds together constitute the quantum equivalent of a triple bond. The orbital and electron dot representations of O_2 and N_2 are shown in Fig. 4.13.

4.4.4 Concept of Hybridisation

Our treatment thus far has been concerned with compounds of hydrogen, flourine, oxygen, and nitrogen. To discuss compounds of carbon, boron and beryllium (restricting ourselves for the time being to the second row elements), two extensions of these principles are required.

The carbon atom has two half-filled $2p$ orbitals (say $2p_x$ and $2p_y$) and one vacant $2p$ orbital ($2p_z$) in its ground state. On the basis of the preceding discussion, one would expect that a carbon atom should form two single bonds. Though compounds like CH_2 are known as transient species, a great majority of the stable carbon compounds are however derived only from the tetravalent carbon atom. Further, chemical and physical evidence reveal that the four bonds of carbon are equivalent and that they are tetrahedrally oriented. These facts can be accounted for by noticing that in the ground state of the carbon atom, there exists a vacant $2p_z$ orbital which has only slightly higher energy

*The classification of orbitals (i.e. σ, π, etc.) on the basis of symmetry is the same in the VB method as in the MO method. However, whereas in the MO method these designations refer to the molecular orbitals, in the VB method they refer to the bond orbitals.

than the fully occupied $2s$ orbital. Had the $2s$ and $2p$ orbitals been of equal energy, then a configuration with four unpaired electrons would have been the ground state, as this would minimise electron repulsion. In the carbon atom, due to the difference in energy of the $2s$ and $2p$ orbitals, the four (unpaired) electron configuration $2s^1 2p^1_x 2p^1_y 2p^1_x$, represents an excited rather than the ground state (Fig. 4.14). It is argued in the VB approach that carbon forms compounds from its excited state. The rationale is that the four half-filled orbitals can form four bonds leading to greater energy-lowering which more than compensates the initial energetically unfavourable situation (in which an electron is in the $2p_z$ orbital rather than the lower energy $2s$ orbital). However, the four bonds formed by carbon after promotion will not be equivalent since one of them involves an s orbital while the other three involve p orbitals. To explain the equivalence of the four bonds, the concept of hybridisation is introduced. *Hybridisation* means, constructing orbitals which do not have pure s or p character but a mixed character. From one s- and three p-orbitals, one can construct four equivalent hybrid orbitals designated

Fig. 4.14 (*a*) The ground state and (*b*) the excited state configuration of the carbon atom

as sp^3 orbitals (Fig. 4.15). These orbitals are found to point toward the four corners of a regular tetrahedron, thus explaining the shape of molecules like CH_4, CCl_4, etc. The justification for hybridisation is that hybrid orbitals concentrate electron density in definite directions much more effectively than pure orbitals, resulting in a greater overlap and hence stronger bonds.

4.4.5 Examples of Hybridisation

Promotion-cum-hybridisation suffices to explain the nature of compounds formed by boron and beryllium. In boron, the ground state configuration is $1s^2 2s^2 2p_x^1$ (Fig. 4.16a). If one of the $2s$ electrons is promoted to the slightly higher energy $2p_y$ orbital, the configuration $1s^2 2s^1 2p_x^1 2p_y^1$ would result (Fig. 4.16b). The three equivalent hybrid orbitals formed from one s- and

Fig. 4.15 The four sp^3 hybrid orbitals formed from one s- and three p-orbitals

two p-orbitals are called sp^2 hybrid orbitals. Their maxima lie towards the corner of an equilateral triangle (see Fig. 4.17). Thus boron should form three bonds with a bond angle of 120° as it does in BF_3. In beryllium, promotion (Fig. 4.18) and hybridisation (Fig. 4.19) lead to two equivalent sp hybrid orbitals which make an angle of 180° with each other. Beryllium compounds like BeH_2 with linear geometry are thus consistent with this interpretation. Properties of these hybrid orbitals are summarised in Table 4.2.

In the third period, with the availability of low-lying vacant $3d$ orbitals, higher covalencies of five and six become possible. In the second row, the maximum possible covalence is four as in carbon. Phosphorus and sulphur have five and six electrons respectively in the $3s$- and $3p$-orbitals. In the ground state, their

Fig. 4.16 (a) The ground state and (b) the excited state configuration of the boron atom
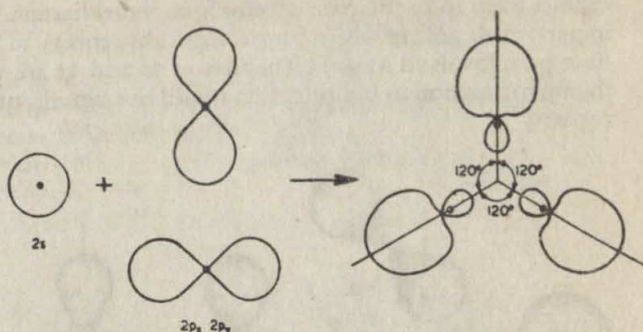
Fig. 4.17 The formation of the three sp^2 hybrid orbitals from one s- and two p-orbitals
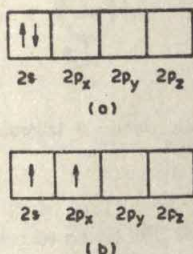
Fig. 4.18 (a) The ground state and (b) the excited state configuration of the beryllium atom
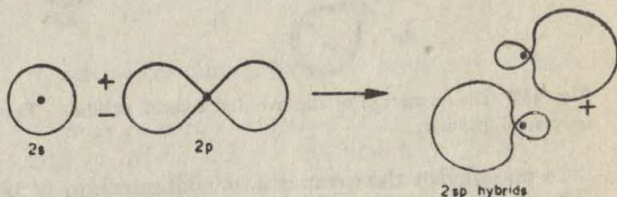
Fig. 4.19 The formation of the two sp hybrid orbitals from one s- and one p-orbital

atoms have (like nitrogen and oxygen) three and two half-filled orbitals. Thus they form compounds like PF_3 and H_2S which are analogous to NF_3 and H_2O. But, phosphorus and sulphur also form compounds like PF_5 and SF_6. The pentavalency of phosphorus and the hexavalency of sulphur becomes possible because all the valence electrons of these atoms can become unpaired by promotion of electrons to the vacant $3d$ orbitals which are comparable in size and energy to the $3s$- and $3p$-orbitals. We would like to emphasize that it is not just the comparable energy but also the comparable size of the $3d$ orbitals that

Table 4.2 Properties of Hybrid Orbitals

Name	s-character	p-character	Bond-Angle	Geometrical arrangement	Examples of molecules
sp digonal	$\frac{1}{2}$	$\frac{1}{2}$	180°	Linear	BeH_2, $HgCl_2$, C_2H_2
sp^2 trigonal	$\frac{1}{3}$	$\frac{2}{3}$	120°	coplanar triangular	BF_3, NO_3^-, C_2H_4, CO_3^{--}
sp^3 tetrahedral	$\frac{1}{4}$	$\frac{3}{4}$	109°	tetrahedral	BH_4^-, NH_4^+, CH_4, ClO_4^-, $SnCl_4$.

enables them to participate effectively in hybridisation. Had only energy been important, $4s$ and $4p$ which have comparable energy to $3d$ in these atoms could have been involved as well. The sizes of $4s$ and $4p$ are very different and thus their participation in hybridisation would not significantly improve the overlap capacity.
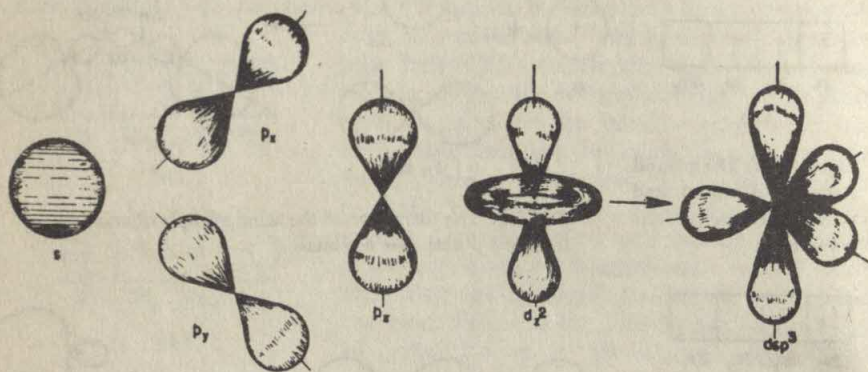
Fig. 4.20 The formation of the five dsp^3 hybrid orbitals. These orbitals define a trigonal bipyramid geometry.

In phosphorus the ground state configuration is $3s^2 3p_x^1 3p_y^1 3p_z^1$. The pentavalent compounds form through the excitation of one of the $3s$ electrons to the $3d_{z^2}$ orbital. The five sp^3d hybrid orbitals have their maxima pointing to the vertices of a trigonal bipyramid (Fig. 4.20). The five orbitals are not equivalent but fall into two groups: one group of three orbitals lying in a plane with their maxima towards the vertices of an equilateral triangle and the other group of two equivalent orbitals pointing perpendicularly above and below the equatorial plane. Experimentally, both these features are found in PCl_5 with the equatorial chlorines being closer to the central phosphorus atom than the out-of-plane chlorine atoms. In sulphur, two electrons are promoted to d_{z^2} and $d_{x^2-y^2}$ orbitals. The maxima of sp^3d^2 hybrid orbitals defines a regular octahedron. These conclusions have been verified in SF_6.

The structures of many polyatomic molecules with multiple bonds can be described using the concepts of σ and π bonds, and of hybrid orbitals. Ethylene (C_2H_4) and acetylene (C_2H_2) which are representative hydrocarbons of the alkene and alkyne series are two good examples (see Chapter 5). Ethylene has a planar structure with bond angles of 120° (Fig. 4.21a). This strongly suggests that the $2s$, $2p_x$ and $2p_z$ orbitals on each carbon atom form three sp^2 orbitals (six hybrids, in all) 120° apart in the molecular plane. Four of these orbitals are utilised to form four C—H bonds by overlapping with the $1s$ orbitals of the hydrogen atoms. The remaining two hybrid orbitals on the two carbon atoms mutually overlap to provide a σ type C—C bond. This leaves two half-filled $2p_y$ orbitals, normal to the molecular plane, which laterally overlap to form another C—C bond of the π variety. These features are shown in Fig. 4.21(b). Thus, our analysis shows that in ethylene there should be four single C—H bonds and one C = C double bond in agreement with experiment. Also, it is obvious that the lateral overlap of $2p_y$ orbitals will be maximum only when the two —CH_2 groups are planar. This means that rotation around a

Fig. 4.21 (*a*) The geometry and (*b*) the orbital overlap pattern in ethylene. The concentric circles represent the 1*s* orbitals of the hydrogen atoms which overlap with the *sp*² hybrid orbitals of the carbon atoms. The two *p* orbitals on the two carbon atoms overlap forming the π bond.
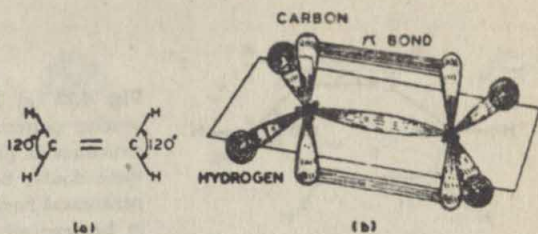
Fig. 4.22 (*a*) The geometry and (*b*) the orbital overlap pattern in acetylene
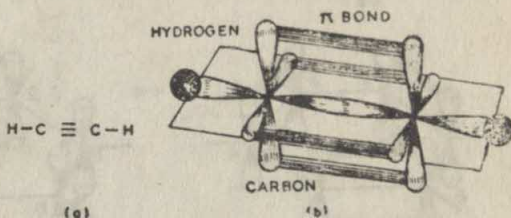
double bond is restricted, a conclusion that had earlier been derived from chemical evidence.

In acetylene (Fig. 4.22) the linear geometry suggests *sp* hybridisation on each carbon atom. Two of the four *sp* hybrid orbitals (formed from 2*s* and 2*p_x* orbitals) overlap with the 1*s* orbitals of hydrogen atoms to give two C—H bonds, while the remaining two *sp* hybrids mutually overlap to form a C—C bond. The 2*p_x* and 2*p_y* orbitals on each carbon atom overlap with the corresponding orbitals on the other carbon atom to form two bonds of the π type. Thus, acetylene has a triple bond between the carbons and two single bonds between the carbon and hydrogen atoms.

It is interesting that the distance between two carbon atoms held together by a single bond is longer than those held together by a double bond. The C—C distance in a double bond in turn is longer than that in a triple bond. Some important properties of hydrocarbons involving different hybridisations of carbon are given in Table 4.3. We see that bond strength varies in reverse order of bond distances; the shorter the bond the greater is its strength or dissociation energy.

Table 4.3 Properties of Hydrocarbons with Hybridisations

Property	$H_3C—CH_3$ *Ethane*	$H_2C=CH_2$ *Ethylene*	$HC≡CH$ *Acetylene*
C—H distance (A)	1·09	1·07	1·05
C—C distance (A)	1·54	1·33	1·20
C—C bond dissociation energy (kcal/mol)	83	143	194
Carbon hybridisation	*sp*³	*sp*²	*sp*

4.4.6 Concept of Resonance

The geometry of benzene is hexagonal and there is sufficient physico-chemical evidence to establish that all the C—C bonds in it are equivalent (Fig. 4.23*a*).
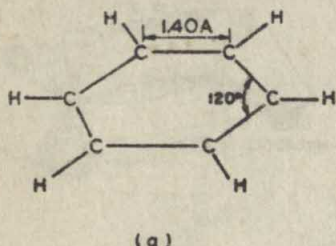
Fig. 4.23 (*a*) The geometry and (*b*) the orbital overlap pattern in benzene. In each of the two structures in (*b*), there are three single bonds and three double bonds which is contrary to the experimental finding that all the C—C bond lengths in benzene are equal to each other (1·40 A).

(a)

(b)
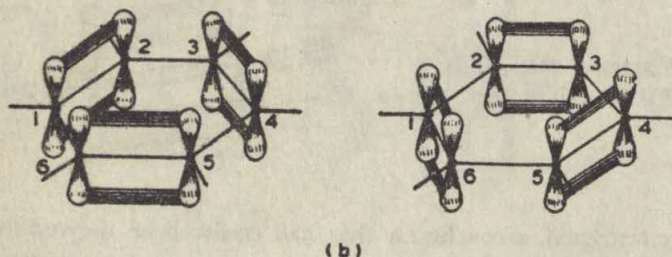
The 120° bond angle again suggests sp^2 hybridisation of the three hybrid orbitals on each carbon atom; two can be used for overlap with the hybrid orbitals of the neighbouring carbon atoms and the third can overlap with the 1*s* orbital of a hydrogen atom. All of these are σ bonds. This leaves six $2p_y$ orbitals perpendicular to the molecular plane. We can combine them in two different ways (Fig. 4.23*b*), but either way benzene would be expected to have three single and three double bonds. This contradicts the experimental fact that all the six C—C bonds are equivalent. Further, x-ray measurements show that the C—C bond distance in benzene (1·40 A) lies between a single bond (1·54 A) and a double bond (1·33 A) length. This means that the C—C bonds in benzene are neither pure single bonds nor pure double bonds. To overcome this difficulty, the VB method introduces the *resonance* concept according to which if two (or more) alternate structures can be written for a molecule, then the actual behaviour of the molecule is described by taking into account all the structures simultaneously. For benzene, this means that neither structure I nor structure II (Fig. 4.24) by itself provides a correct description, but only a combination (hybrid) of the two does. Since I has single bonds where II has double bonds (and vice-versa), the two structures jointly imply one-and-half bonds between all pairs of carbon atoms in benzene (thus making them equivalent) as experiments demand. The resonance idea is frequently expressed in the form: Benzene resonates between the two structures or benzene is a resonance hybrid of the two structures. This type of expression should not be
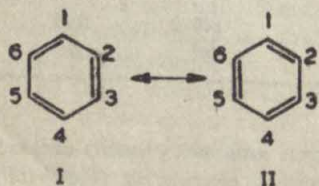
Fig. 4.24 I and II are two (primary) resonance structures of benzene. The molecule is (primarily) the resonance hybrid of these structures.
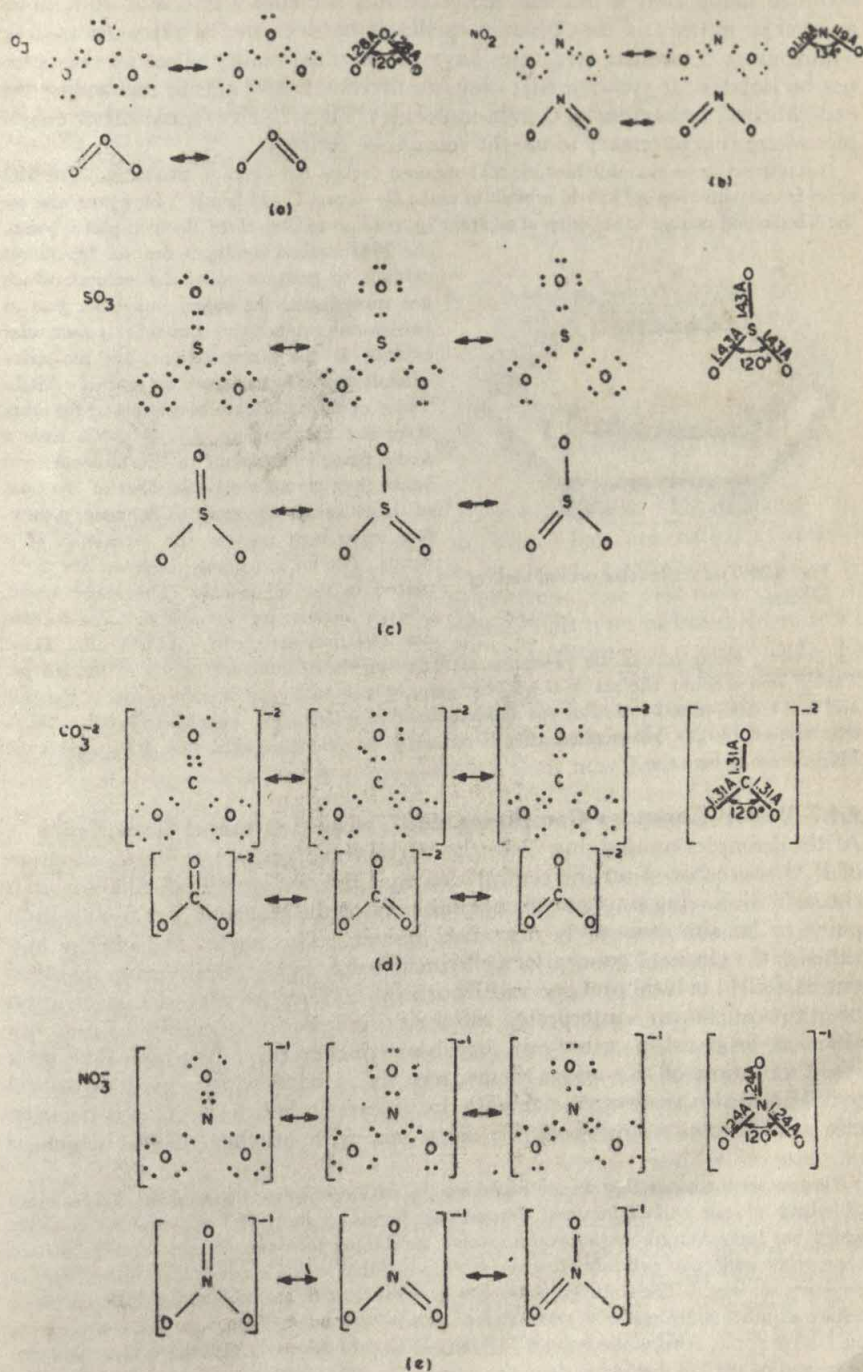
Fig. 4.25 Resonance in some molecules and ions

taken to mean that a benzene molecule has sometimes one and sometimes another structure and that benzene oscillates between the two structures. The contributing resonance structures have no physical reality (that is, they cannot be isolated or synthesised); they are merely mental aids to rationalise the experimental behaviour of certain molecules. Fig 4.25 gives some other examples where it is necessary to use the resonance concept.

It is instructive to examine how the MO method tackles the benzene problem. The MO approach also involves sp^2 hybrid orbitals to make C—C and C—H bonds.* However whereas the VB method utilises the overlap of adjacent $2p_y$ orbitals to form three electron-pair π bonds,

the MO method combines the six $2p_y$ atomic orbitals to generate molecular orbitals which are spread over the entire molecule. Just as two atomic orbitals give rise to two molecular orbitals in the diatomic case, six molecular orbitals can be formed from six atomic orbitals. Three of these MOs are bonding and the other three are anti-bonding. All the MOs have a nodal plane in the plane of the molecule and hence they are all π orbitals. Out of the total of thirty valence electrons in benzene, twenty-four have been used in the formation of σ bonds. The six remaining electrons are to be placed in the π orbitals. The three lowest orbitals (all bonding) are able to accommodate two electrons each with opposite spin. These

Fig. 4.26 The molecular orbital view of benzene

six bonding electrons can be viewed as contributing three additional bonds of the π type. Taking into account the six σ- bonds, one can say that each pair of carbon atoms has one and half bonds—one bond of σ type and half bond of π type. This conclusion is the same as that arrived by the VB method after introducing the resonance idea. Fig. 4.26 depicts the MO picture of benzene.

4.4.7 Donor–Acceptor Complexes and Transition-metal Complexes

All the examples treated thus far by the VB method (with the solitary exception of H_2^+), were based on the central idea that the overlap of half-filled orbitals (i.e. orbitals having single electron) enables both the electrons (i.e. the electron pair) to be simultaneously near two nuclei. This lowers the energy and explains the classical concept of a chemical bond. In H_2^+, the overlap involved one half-filled orbital and one vacant orbital. Here, we placed one electron near two nuclei and interpreted the resulting lowering of energy as due to a one-electron bond, a rather rare occurrence in chemistry. We now take up a slight variation of the above theme, namely, a bond which involves orbital overlap and also an electron-pair with the difference that the overlap is between one orbital containing both the electrons, with another orbital which is

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*It may seem strange that we are beginning the MO description by using the VB language of hybrid orbitals and of localised electron-pair bonds. A strict MO approach to benzene, which has forty-two electrons, would involve combining forty-two atomic orbitals to form appropriate molecular orbitals. However, it turns out that such a complex procedure is neither necessary nor useful. The static geometry of benzene is fixed by the thirty-six σ electrons which behave approximately as if they were localised. Therefore, to describe the geometry of benzene, the VB viewpoint is very convenient. The remaining six electrons (called the π electrons) can be treated by the VB method as done above or by the MO method as we are now doing. The MO description of all polyatomic molecules usually follows a similar procedure.

Fig. 4.27 (*a*) **The** Lewis structure of the BF_3—NH_3 complex. The lone pair on the nitrogen atom (of NH_3) and the vacant valence orbital on the boron atom (of BF_3) are responsible for the bond formation. (*b*) The geometry of the BF_3—NH_3 complex. The BF_3 and the NH_3 molecules get distorted as a result of complex formation.

(a)

(planar, $\angle FBF = 120°$)   (b)
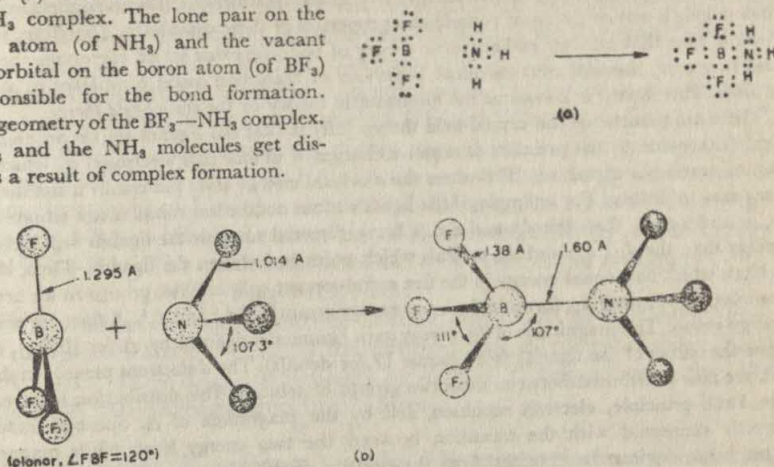
vacant. Such situations arise usually in two contexts. In one case, two otherwise stable molecules combine to form what are called as *molecular complexes*. The essential requirement for bond formation is that one molecule should have an unused pair of electrons (*lone pair electrons*) and the other molecule should have a vacant orbital. This type of bond is sometimes referred to as an *electron donor–acceptor bond* (or sometimes as a *dative bond*). The other case is found to occur in transition-metal chemistry. Here, a metal ion with vacant valence orbitals forms bonds with stable molecular groups (known as *ligands*) having lone pair of electrons. These are usually known as *transition-metal complexes* or *coordination compounds*. We shall now look at an example of each type of complex; many more examples will be discussed later.

Consider the molecules BF_3 and NH_3. As shown earlier, each of the three B—F bonds in BF_3 is formed by the overlap of an sp^2 hybrid orbital of boron with the $2p_z$ orbital of a fluorine atom. This leaves a vacant $2p_z$ orbital on the boron atom. In ammonia molecule, on the other hand, a lone pair is left after the formation of the three N—H bonds. NH_3 and BF_3 can obviously combine to form a molecular complex BF_3—NH_3 in which the nitrogen atom orbital containing the lone pair overlaps with the vacant valence orbital of boron. This results in change in hybridisation of the boron from sp^2 to sp^3. Fig. 4.27 shows the electron dot representation and geometry of this molecular complex.

As an example of transition metal ion complexes, we shall take the general case of octahedral complexes. Specific examples of this type [e.g. $Ti(H_2O)_6^{+1}$, $Co(NH_3)_6^{+3}$, $Fe(CN)_6^{-3}$] as well as the general and specific cases of the complexes with other geometries (e.g. tetrahedral, square planar) will be discussed later in Chapter 17. For octahedral complexes, the VB approach assumes the existence of six vacant d^2sp^3 hybrid orbitals on the central metal ion. These hybrids overlap with suitable ligands (e.g. NH_3, H_2O, CN^-) having lone pair of electrons to form metal complexes. The specific orbitals involved in the hybrids are s, p_x, p_y, p_z, d_{z^2} and $d_{x^2-y^2}$. The VB theory is successful in correlating many properties of the transition metal complexes as will be shown later (Chapter 17).

The inability of the VB method to account for spectra in an elementary way has been pointed out earlier. This deficiency is particularly felt in its treatment of transition metal complexes since colour is one of the most conspicuous properties of these complexes. Therefore, it is satisfying to note that another rather simple theory of bonding exists which correlates the spectra, and magnetic, thermal and chemical behaviour of transition metal complexes in an unified manner. This theory is known as the electrostatic theory or the *crystal-field theory*.

The main premise of the crystal-field theory (cft) is that the ligands set up an electrostatic field (either due to the presence of negative charges or of lone pair electrons) in which sits the central transition metal ion. This alters the d orbital energy level pattern in a manner that is very easy to deduce. For example, if the ligands of an octahedral complex are situated on the x-, y- and z-axes, then the d_{z^2} and $d_{x^2-y^2}$ being directed towards the ligands will have higher energy than the d_{xy}, d_{xz} and d_{yz} orbitals which point in between the ligands. Thus, the five d orbitals which had equal energy in the free metal-ion get split into two groups in an octahedral complex, d_{xy}, d_{xz} and d_{yz} forming the lower energy group and d_{z^2} and $d_{x^2-y^2}$, forming the higher energy group. The magnitude of the energy gap, commonly denoted by Δ (or 10 Dq), depends upon the nature of the ligands (see Chapter 17 for details). The d electrons present in the metal ion are now distributed between these two groups of orbitals. This distribution is governed by the Pauli principle, electron repulsion, and by the magnitude of Δ. Spectral features are directly connected with the transition between the two energy levels while magnetic and other behaviour can be obtained from the electron distribution as in the VB or MO theory.

The weakest link in the cft is that it has nothing to say about the nature of the bond between the central metal ion and the surrounding ligands. This is because the theory operates entirely with the electrostatic effect of the field generated by the ligands on the d orbital energies. This deficiency has been remedied in a more comprehensive theory known as the *ligand-field theory* (lft) which is essentially a molecular orbital approach applied to the transition metal ion complexes (see Chapter 17 for details). The molecular orbital energy levels of a complex are obtained from a combination of suitable metal-ion orbitals and ligand orbitals containing the lone pairs. The choice of the metal-ion orbitals is dictated by the symmetry of the complex. Thus, for octahedral geometry, d^2sp^3 hybrid orbitals of the metal ion are used. The three d orbitals (i.e. d_{xy}, d_{yz}, d_{xz}) not used in hybridisation are called the non-bonding orbitals, whereas the combination of the ligand and the metal-ion orbitals generates, as usual, the bonding and anti-bonding orbitals. The energy gap between the non-bonding and the anti-bonding orbitals plays the same role in lft that Δ does in cft. The bonding orbitals are completely filled by the six pairs of electrons from the ligands in the case of an octahedral complex. The d electrons of the metal ion are distributed between the non-bonding and the anti-bonding orbitals and control the spectral and magnetic properties of the complex.

4.5 POLAR MOLECULES

The idea that the electron pair involved in a bond is equally shared by the two atoms is strictly valid only when the two atoms are identical. If the atoms are different, then they differ in their capacity to attract electrons and this results in unequal sharing of the electron pair. The chemical bond in such a case is called a *polar covalent bond*. It is useful to assign a numerical measure, called *electronegativity*, for the attractive power of an atom for electrons in a bond.

4.5.1 Electronegativity Scale
The formulation of the electronegativity concept can be done by considering two atoms, $A(1)$ and $B(2)$, each containing a single unpaired electron. (In this particular example we label the electron of A by 1 and that of B by 2 to facilitate the argument.*) Now let us assume that these two atoms can form a molecule

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*We must however warn that this is done only for the sake of convenience. Quantum mechanics rules out any way of identifying (and hence labelling) electrons.

$(A \frac{1}{2} B)$ in which the electron pair is shared. If atoms A and B are identical, then it is obvious that the electron pair must be equally shared. However, if the atoms are different, the sharing is unequal. What can we say quantitatively about this unequal sharing, from a consideration of the nature of the two atoms? The answer can be obtained in several ways, but perhaps the simplest is based on the concepts of ionisation energy (IE) and electron affinity (EA).[*]

Let IE_1 and EA_1 be the ionisation energy and electron affinity respectively (of electron 1) of A and IE_2 and EA_2 be the ionisation energy and electron affinity (of electron 2) of B. If the electron of A is transferred to B, the energy change is $IE_1 + EA_2$ while if the electron of B is transferred to A, the energy change is $IE_2 + EA_1$. The condition for equality of these energy changes,

$$IE_1 + EA_2 = IE_2 + EA_1$$

is also the condition for equal sharing because there will be no energy gain even on complete transfer (which is the extreme case of unequal sharing). If $(IE_1 - EA_1)$ and $(IE_2 - EA_2)$ are denoted by X_1 and X_2 respectively, then the above equation can be rearranged in the form

$$X_1 = X_2$$

If X_1 is greater than X_2, it means that the difference between the ionisation energy and electron affinity for the atom A is greater than the corresponding difference for B, that is, A has greater attraction for the shared electron pair than B. If X_2 is greater than X_1, B has a greater share of the electron pair. We thus find that the quantity X of an atom is a measure of its attraction for an electron. This quantity is called the *electronegativity* of an atom. The higher the electronegativity, the greater is the attraction. In practice, electronegativity of an atom is defined by the relation

$$X = (IE - EA)/5 \cdot 6$$

The factor $1/5 \cdot 6$ is a constant of proportionality[†] which is introduced so that the electronegativity numbers obtained this way agree with the numbers obtained from other considerations. Table 4.4 gives the commonly accepted

Table 4.4   Electronegativities of Some Elements

H						
2·1						
Li	Be	B	C	N	O	F
1·0	1·5	2·0	2·5	3·0	3·5	4·0
Na	Mg	Al	Si	P	S	Cl
0·9	1·2	1·5	1·8	2·1	2·5	3·0
K	Ca	Ga	Ge	As	Se	Br
0·8	1·0	1·6	1·7	2·0	2·4	2·8
Rb	Sr					I
0·8	1·0					2·4
Cs	Ba					
0·7	0·9					

values of electronegativity for various elements. It should be remembered that the electronegativity of an element is a relative, and not an absolute measure of the attraction for electrons.

[*]Recall that IE is the energy needed to remove an electron and EA is the energy released on capturing an electron.

[†]The factor $1/5 \cdot 6$ is used when IE and EA values are expressed in electron volts.

Example 4.1 Calculate the electronegativity of the chlorine atom.

From Tables 3.6 and 3.7, IE of $Cl = 13 \cdot 0$ ev and EA of $Cl = -4 \cdot 01$ ev.

$\therefore X_{cl} = 17 \cdot 01 / 5 \cdot 6 \approx 3 \cdot 0$

Electronegativity values show periodic variation. Within a group or family electronegativity generally decreases with increasing atomic number. In the transition element groups there is usually only a slight variation in the electronegativity values. As we pass from element to element in a horizontal row across the periodic table, the general trend is toward increasing electronegativity. These trends are in agreement with those of the ionisation energies and electron affinities. Low electronegativity is characteristic of metals. The lower the electronegativity, the more active the metal. Thus the lowest electronegativities are found at the lower left of the periodic table. High electronegativity is characteristic of non-metals. Thus the highest electronegativities are found at the upper right of the periodic table. Flourine is the most electronegative element followed by oxygen. The noble gases do not normally form chemical bonds and hence are not assigned electronegativity values.

4.5.2 Bond Moment and Molecular Dipole Moment

A consequence of the unequal sharing of electrons is that the bond acquires polar character (i.e. one end becomes positive and the other negative) since the electron pair is asymmetrically located between the two atoms.* The polar character of bonds increases as the electronegativity difference increases. Table 4.5 gives the relation between the two. This means that a bond dipole

Table 4.5 Polar Character of Bonds and Electronegativity Difference

$X_A - X_B$	Polar character %	$X_A - X_B$	Polar character %	$X_A - X_B$	Polar character %
0·0	0	0·8	12	1·8	47
0·2	1	1·0	18	2·0	54
0·4	3	1·4	32	2·2	61
0·6	7	1·6	40	2·4	68

moment, or bond moment in short, can be associated with a chemical bond. *Bond moment* is a vector quantity because it has magnitude as well as direction. The magnitude of bond moment, μ, is given by the product of the charge, q, at either end and the distance of separation (r) between the opposite charges (i e. $\mu = qr$). The unit for expressing the magnitude of molecular *dipole moment* is called a debye (denoted by D), in honour of Peter Debye who contributed much to our understanding of polar molecules. One debye is equal to

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*Another consequence is that the bond becomes more stable since the electrons are closer to the atom which attracts it more. The original electronegativity scale was constructed by Pauling by comparing dissociation energies (which are a measure of stability) of homonuclear diatomic molecules with those of heteronuclear diatomic molecules. The mathematical form of *Pauling's relation* is $\epsilon_{A-B} = \frac{1}{2}\epsilon_{A-A} + \frac{1}{2}\epsilon_{B-B} + 23 (X_A - X_B)^2$ where ϵ_{A-B}, ϵ_{A-A} and ϵ_{B-B} are the dissociation energies of the corresponding molecules in kcal/mol. Since we have developed the electronegativity scale using Mulliken's approach, we shall reverse Pauling's arguments and use his relation to estimate bond energies as discussed in section 4.9.

10^{-18} esu.cm. If two equal but opposite charges, each having magnitude equal to the electron charge (4.8×10^{-10} esu) are separated by a distance of 1A then the dipole moment has the value 4.8D. The direction of μ is conventionally indicated by drawing an arrow from the positive end of the dipole to the negative end (see Fig. 4.28). If a molecule has only one bond, then the bond moment is also the molecular dipole moment, but in a polyatomic molecule the molecular moment is the resultant of the bond moments. Since the resultant depends upon the magnitude and the relative orient- ation of bond moments, there exists an intimate connection between molecular geometry and molecular dipole moment.

Fig. 4.28 A dipole. The direction of the dipole moment is defined by an arrow which points from the positive end to the negative end.

Amongst diatomic molecules, only the hetero- nuclear type have dipole moments. The measured values in these cases permit estimation of ionic character of the bond.

Example 4.2 Calculate the percentage ionic character in HCl molecule. The bond distance of HCl is 1.275 A and the observed dipole moment is 1.03 D.

For complete transfer of an electron (i.e. 100 per cent ionic character) the dipole moment should be

$$\mu_{calc} = 4.8 \times 10^{-10} \times 1.275 \times 10^{-8} = 6.11 \text{ D}$$

The observed dipole moment is only 1.03 D. Hence,

$$\text{percentage ionic character} = \frac{1.03}{6.11} \times 100 = 17\%$$

In triatomic molecules, both the angular (e.g. H_2O) and the linear asym- metric (e.g. N_2O) types have dipole moments. In the linear symmetric mole- cules (e.g. CO_2), the two equal bond moments point in opposite directions and

(a)

(b)

(c)
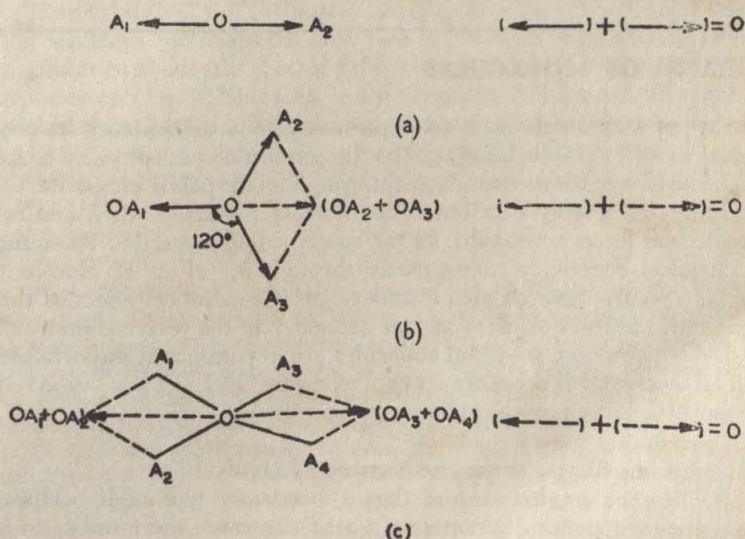
Fig. 4.29 Vector addition of bond moments for some geometries. A_1, A_2, A_3 and A_4 are identical atoms.

cancel each other as shown in Fig. 4.29(*a*). Such molecules, therefore, do not have dipole moments. Tetratomic molecules with triangular geometry as in Fig. 4.29(*b*), (e.g. BF_3), pentatomic molecules with tetrahedral geometry as in Fig. 4.29(*c*) (e.g. CH_4) and heptatomic molecules with octahedral geometry (e.g. SF_6) also do not possess dipole moments since the resultant of the bond moments for these geometries is zero. However, tetratomic molecules with pyramidal structure (e.g. NH_3) have net dipole moment. One can work out for various geometries whether dipole moment should exist or not and this can in many cases provide a clue to molecular shapes. Table 4.6 gives dipole moment data on molecules of various shapes.

Table 4.6 Molecular Shape and Dipole Moment

Molecule	Shape	Dipole Moment, D	Classification	Molecule	Shape	Dipole Moment, D	Classification
CS_2	Linear	~0	Non-polar	PF_3	Trigonal pyramidal	1·03	Polar
HCN	Linear	2·95	Polar	AsF_3	Trigonal pyramidal	2·82	Polar
OCS	Linear	0·71	Polar	H_2O	Angular	1·844	Polar
BF_3	Trigonal planar	~0	Non-polar	H_2S	Angular	0·92	Polar
SO_3	Trigonal planar	~0	Non-polar	SO_2	Angular	1·633	Polar
CF_4	Tetrahedral	~0	Non-polar	NO_2	Angular	0·39	Polar
CCl_4	Tetrahedral	~0	Non-polar	O_3	Angular	0·52	Polar
NH_3	Trigonal pyramidal	1·47	Polar				

4.6 SHAPES OF MOLECULES

The shape of a molecule plays an important role in determining its physical, chemical, as well as biological functions. Its connection with physical characteristics like surface tension, viscosity, melting and boiling points, etc., arises because shape influences charge distribution in molecules which in turn controls the intermolecular forces responsible for the macroscopic properties. Its connection with chemical reactivity comes partly through the effect of charge distribution and partly through such factors as steric hindrance (effect of the bulk of molecules), mutual orientation and geometry of the reacting molecules. In biological phenomena, shapes of molecules are of paramount importance since almost all biochemical processes are controlled by ' lock and key ' type relationships between the shapes of reactants and products.

4.6.1 Deducing Shape from the Nature of Orbitals

We stated earlier in this chapter that a particular type of hybridisation is associated with a definite geometry. In all these cases, the number of hybrid orbitals is equal to the number of bonds. Let us examine a few molecules where the number of hybrid orbitals is greater than the number of bonds. Consider the molecule H_2O. If we assume that the oxygen atom (like the carbon atom)
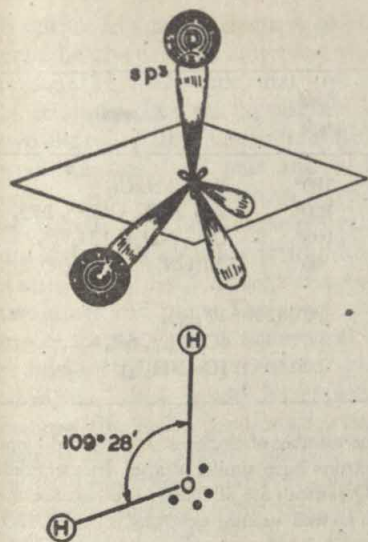
Fig. 4.30 If sp^3 hybridisation is assumed for the oxygen atom, the predicted angle in H_2O should be 109° 28′
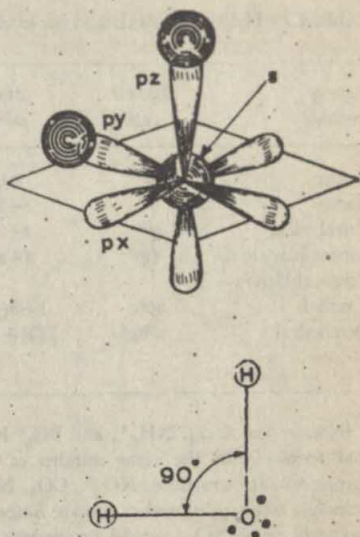
Fig. 4.31 If the O—H bonds in water are assumed to involve pure p orbitals on the oxygen atom, then the predicted angle in H_2O should be 90°

also forms sp^3 bonds, the six valence electrons of the oxygen atom have to be accommodated in these four hybrid orbitals. Two of these hybrid orbitals will each have a pair of electrons with opposite spins and the other two will each have one unpaired electron. Thus oxygen atom can form two bonds by overlap with the 1s orbitals of two hydrogen atoms and the H—O—H angle should be 109°28′ which is the angle between two sp^3 orbitals (Fig. 4.30). The experimental value of about 105° is reasonably close to the predicted value. The slight discrepancy can be explained by noting that the two lone pairs should repel each other thus distorting the regular tetrahedron and leading to a contraction of the HOH angle. Similar analysis for NH_3 predicts that the H—N—H angle should also be 109°28′ which is quite close to the experimental value of about 107°. Table 4.7 summarises some of the common hybrids and the corresponding shapes.

The shapes of H_2O and NH_3 can also be explained without invoking the hybridisation idea. It has been shown that the $2p_y$ and $2p_z$ orbitals of the oxygen atom (each containing an unpaired electron) overlap with two hydrogen 1s orbitals, also containing unpaired electrons, to form the two O—H bonds. Since the $2p_y$ and $2p_z$ orbitals are oriented perpendicular to each other, it follows that the HOH angle should be 90° (Fig. 4.31). The same reasoning leads to the 90° angle in H_2S and H_2Te as well. However, whereas the observed angle of 92° for H_2S and H_2Te agree well with the predicted value, the observed angle of 104° for water shows considerable discrepancy. The reason for this deviation is easy to comprehend. The O—H bond is a fairly polar bond because there is significant difference between the electronegativity of the oxygen atom (3·0) and that of the hydrogen atom (2·1). Consequently, charge separation takes place resulting in the oxygen atom acquiring a fractional negative charge and the hydrogen atom acquiring a fractional positive charge. The two positively charged hydrogen atoms repel each other, causing the HOH angle to widen from its expected value of 90°. This

Table 4.7 Hybrid Orbitals and Molecular Shapes

Shape of molecule	Hybrid type	Atomic orbitals	Bond angle	Examples
Linear	sp	$s+p$	180°	$BeCl_2$, $HgCl_2$
Planar	sp^2	$s+2(p)$	120°	BF_3, BCl_3, CO_3^{2-}, NO_3^-
Tetrahedral	sp^3	$s+3(p)$	109°	CH_4, NH_4^+, BH_4^-([1])
Square planar	dsp^2	$d+s+2(p)$	90°	$Ni(CN)_4^{2-}$, $PtCl_4^{-2}$
Trigonal bipyramidal	sp^3d	$s+3(p)+d$	90°, 120°	$PF_5(g)$
Octahedral	d^2sp^3	$2(d)+s+3(p)$	90°	$[CrF_6]^{-3}$, SF_6 $[Co(NH_3)_6]^{+3}$

[1]Notice that CH_4, NH_4^+, and BH_4^- have the same number of electrons. It is indeed found that species with the same number of valence electrons have similar shapes (isoelectronic principle). For example, NO_2^+, CO_2, N_3^- and NCO radicals are all linear. We can use this principle to roughly predict shapes. Since NO_2^+ with sixteen valence electrons is linear, NO_2 has to be bent; NO_2^- would also be bent just as O_3.

reasoning also explains why the bond angles in H_2S and H_2Te do not show much deviation from 90°. In both these cases, the electronegativity difference is small, causing much less charge separation and therefore, much less widening of the angle.

A similar argument would also apply to the NH_3 molecule. Here, the three N—H bonds are formed from overlap of the $2p_x$, $2p_y$ and $2p_z$ orbitals of the nitrogen atom with the 1s orbitals of three hydrogen atoms. The orientation of the three 2p orbitals shows that the hydrogen atoms must be situated at equal distances in three mutually perpendicular directions. In other words, the NH_3 molecule should be pyramidal with the nitrogen at the apex, and the three hydrogens forming the base of the pyramid. The HNH angle should be 90°. Again, the observed angle of 107°, which shows a slight deviation, can be explained by taking into account the electronegativity difference between nitrogen and hydrogen atoms and the consequent polar character of the N—H bond.

4.6.2 Electron-pair Repulsion Method

Though the nature of orbitals provides a clue to the shapes of molecules in many instances, the simplest approach to the problem of shapes is based on the so-called valence-shell electron-pair repulsion (epr) method. The underlying idea of this method is that since like charges repel, two electron pairs stay as far apart as possible. This is really a form of the minimum energy principle and is sufficient to predict shapes of a variety of polyatomic molecules.

The application of the epr method is very straightforward. A molecule with two valence electron pairs (e.g. BeH_2, $HgCl_2$) will obviously prefer a linear geometry, as this places the electron pairs at maximum possible distance. For a molecule with three electron pairs (e.g. BF_3), the optimum arrangement places the pairs at the three vertices of an equilateral triangle. The tetrahedral structure (e.g. CH_4) minimises the repulsion for four electron pairs. In the same manner, trigonal bipyramid and octahedral geometries are predicted for five and six electron pairs respectively, as observed in the case of PF_5 and SF_6. These results are illustrated in Fig. 4.32.

In all the cases we have considered, we have taken into account only the valence electron pairs which participate in bonding (shared electron pairs).

If unshared valence electron pairs are also present in a molecule, then they too must be considered. However, since unshared pairs are more exposed, it seems reasonable to assume that the repulsion between two unshared pairs will be stronger than the repulsion between two shared pairs. The interaction between an unshared pair and a shared pair would be expected to have intermediate magnitude. These expectations are supported by experimental findings. Thus, XeF_4 has four shared pairs and two unshared pairs. The optimum geometry for six pairs is octahedral. Since repulsion between unshared pairs is strongest, they would be expected to occupy the axial positions leaving the four planar positions for the shared pairs. This means that XeF_4 should be square planar as confirmed by experiment (Fig. 4.33a). In XeF_2, there are five electron-pairs which favour a bipyramidal distribution. The three unshared pairs should occupy the equatorial positions while the shared pairs should take the axial positions. This makes XeF_2 a linear molecule (Fig. 4.33b) in agreement with experiment. The extension of this method to double-bonded systems can be made by assuming that the double bond occupies the place of an electron pair. This is

Fig. 4.32 The various geometries based on the electron pair repulsion model. In each case the given arrangement minimises the electron pair repulsion.

reasonable since in the $\sigma-\pi$ description of bonding, only the σ bonds determine the geometry of a molecule. Thus, in ethylene, this assumption means that there are three electron-pairs around each carbon which should, therefore, make the HCH angles 120°. In Table 4.8 we have summarised the shapes of various molecules having different number of shared and unshared pairs.

Fig. 4.33 The geometry of (a) XeF_4 and (b) XeF_2 on the basis of the electron pair repulsion model.
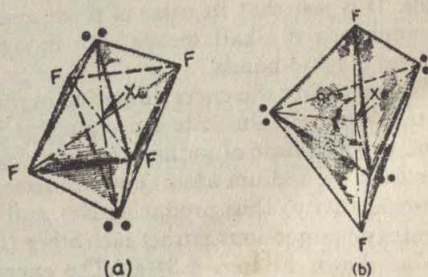
4.7 ION-PAIR MOLECULES

As discussed earlier in section 4.6, a bond in which there is unequal sharing of electron pair is called a polar covalent bond. This happens wheneve. the

Table 4.8 Shapes of Molecules from Electron Pair Repulsion Model

Number of electron pairs	Arrangement	Number of bond pairs	Number of unshared pairs	Shape of molecule	Example
2	Linear	2	—	Linear	$HgCl_2$
3	Triangular	3	—	Planar (120° bond angles)	BCl_3
		2	1	V-shape	$SnCl_2$ (gas)
4	Tetrahedral	4	—	Tetrahedral	CH_4
		3	1	Pyramidal (trigonal)	NH_3
		2	2	V-Shape	H_2O
5	Trigonal bipyramid	5	—	Trigonal bipyramid	PCl_5
		4	1	Irregular tetrahedron	$TeCl_4$
		3	2	T-shape	ClF_3
		2	3	Linear	XeF_2
6	Octahedral	6	—	Octahedral	SF_6
		5	1	Square pyramid	IF_5
		4	2	Square planar	XeF_4
7	Pentagonal bipyramid	7	—	Pentagonal bipyramid	IF_7

electronegativities of the two atoms forming the bond are different. However, if the difference is very large, sharing becomes so unequal that the electron pair can become the exclusive possession of one of the atoms. In such situations it would be reasonably correct to say that an electron has been transferred from one atom of lower electronegativity, to another atom with higher electronegativity.[*] The transfer creates positive and negative ions and such a bond is called an *ionic bond*. The resulting ' molecule ' contains ions and not atoms, and is, therefore, more appropriately termed as an ion-pair. We must emphasize that there is no sharp boundary separating polar covalent bonds from ionic bonds. It is just that in cases of pronounced electronegativity difference (e.g. in compounds of alkali metals with halogens), it is more convenient to think in terms of ionic bonds.

Understanding the energy lowering in (or the stability of) ion-pairs is a simple matter. We shall illustrate the argument for the ion-pair Na^+Cl^- which exists in the vapour phase of sodium chloride. Electron transfer in this ion-pair takes place from the sodium atom (low electronegativity) to the chlorine atom (high electronegativity) thus producing Na^+ and Cl^- ions (Figs. 4.34a and b). These oppositely charged ions attract each other (following the well-known Coulomb's law) as shown in Fig. 4.34(c). The energy requirements of the three steps namely, removal of an electron from the sodium atom (i.e. the ionisation energy of the sodium atom), the electron gain by the chlorine atom (i.e. the electron affinity of chlorine atom), and the potential energy of Na^+—Cl^- ion-pair

[*]No case is known in which complete transfer of an electron (i.e. 100 per cent) takes place.

Fig. 4.34 The formation of Na$^+$Cl$^-$ ion-pair. (a) Na and Cl atoms are at infinite distance. (b) The transfer of an electron from a sodium atom to a chlorine atom resulting in the formation of Na$^+$ and Cl$^-$ ions. The energies involved in the transfer process are as shown. (c) The attraction between the oppositely charged ions results in the formation of the ion-pair. The minimum in the energy occurs when the separation is 2.38 A.
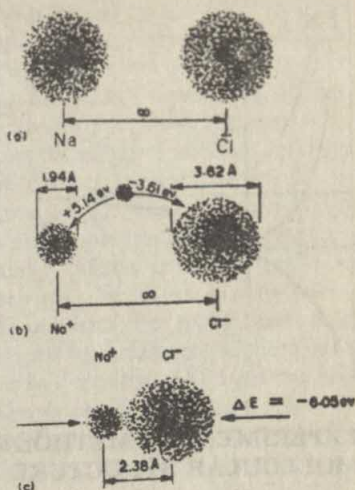
for the equilibrium distance (2·38 A), are either measurable or calculable. Their values are:

$Na(g) \rightarrow Na^+(g) + e$	$\triangle E = IE$	$= 118.5$ kcal/mol (5·14ev)
$Cl(g) + e \rightarrow Cl^-(g)$	$\triangle E = -EA$	$= -83.2$ kcal/mol ($-3\cdot61$ev)
$Na^+(g) + Cl^-(g) \rightarrow Na^+ - Cl^-(g)$	$\triangle E$	$= -139.5$ kcal/mol($-6\cdot05$ev)

$$Na(g) + Cl(g) \rightarrow Na^+ - Cl^-(g) \qquad \triangle E = -104.2 \text{ kcal/mol } (-4.52 \text{ ev})$$
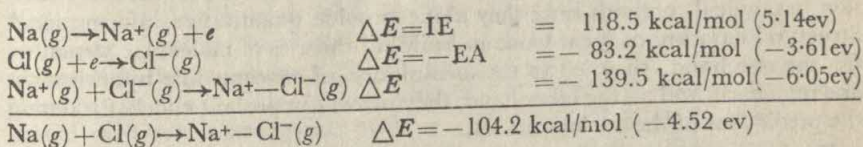
We see that the ion-pair is more stable than the isolated atoms by -4.52 ev. It can be clearly seen that it is the coulomb attraction between oppositely charged ions that is the source of energy lowering; the first two steps *together*, which represent the transfer of electron or formation of ions, are not favoured on energetic grounds.

An obvious question that arises is, if oppositely charged sodium and chlorine ions attract each other, why do they not come closer than 2·38 A? The answer to this question is that at large distances the interaction between oppositely charged ions is attractive, but as the ions get closer, the outer orbitals start penetrating into each other and the nuclei of the ions begin to feel each other's influence. Since the nuclei carry the same charge, their interaction is repulsive. The general variation of attractive, repulsive and the total energy of interaction of any pair of oppositely charged ions as a function of distance between them is of the form shown in Fig. 4.35. The equilibrium distance corresponds to the minimum r_0 in the curve for the total energy; at this point, the repulsive and attractive forces balance each other.

From a chemical point of view, ion-pair molecules are not very important since at ordinary temperatures they condense to give ion aggregates either in liquid or solid form. However, the ionic bond plays a key role in controlling the properties of such solids and liquids. It is easy to visualise how cations and anions alternately placed in rows in three dimensions would stabilise the system by electrostatic attractive forces alone. We shall be dealing with ionic solids at some length in Chapter 7.
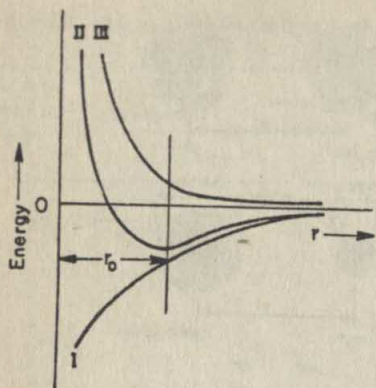
Fig. 4.35 The energy of a typical ion-pair as a function of internuclear separation. (I) represents the energy contribution due to attraction. This monotonically decreases as the ions come closer and closer. (III) represents the energy contribution due to repulsion. This is nearly zero for large distances but at small distances it increases rapidly. The repulsion arises due to interaction of similarly charged nuclei of the two ions. (II) represents the total (i.e. attraction plus repulsion contribution) energy. This curve shows a minimum at r_0 which is the equilibrium separation of the ion-pair.

4.8 EXPERIMENTAL METHODS FOR DETERMINING MOLECULAR STRUCTURE

In this section, we shall briefly examine some of the experimental methods used for determining the structural features of molecules like bond distance, bond angle, force constant and molecular shape. We shall restrict the discussion to physical methods since they alone provide quantitative information.* Structural data are of great value in building theories of molecular structure. On the one hand, they led to the formulation of concepts like hybridisation and resonance, and on the other hand, they provide important checks for testing the predictions of the various models.

Physical and chemical methods together are widely used for qualitative purposes also, like finding functional groups and other specific structural features, and establishing the purity and identity of compounds. Some other uses of these methods are for quantitative estimation of substances (in micro scale) and for studying rates of reactions.

We would like to emphasize that there is no single method or even a single procedure that is of universal applicability. Every molecule presents its own special problems and hence every molecule has to be tackled differently. The first step in structure analysis is to determine the empirical and the molecular formula of the molecule. Some of the methods for doing this were mentioned in Chapter 2. A modern chemist then employs a variety of techniques to pinpoint the structure of a given molecule, but it is not possible to discuss all of them here. We shall describe only those methods which are generally useful.

4.8.1 Mass Spectrometry

When molecules are bombarded by high energy electrons or are subjected to an electric discharge, they tend to lose one or more electrons forming different kinds of positive ions. The bonds in the molecule are also ruptured thus producing

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*Chemical methods can provide information on molecular shapes and hence indirectly, the bond angles. Indeed, the classic researches of Kekule, Fischer and Werner which established the geometry of benzene, the tetrahedral nature of carbon valences and the geometry of coordination compounds, were entirely based on chemical methods. However, modern developments have made this approach obsolete.

fragments which too acquire positive charge by losing electron(s). These ions are generally unstable but live long enough to be accelerated into the magnetic field of a mass spectrometer. (The principle of operation of a mass spectrometer was given in Chapter 3 in connection with Thomson's experiment.) The extent of their deflection in the field depends upon their mass/charge (m/e) ratio. Different ions collect at different spots and the series of such peaks constitutes the mass spectrum. The relative peak heights correspond to the relative amounts of different fragments. The highest peak at the largest mass is usually due to the positive ion formed from the parent molecule and therefore gives the exact molecular mass of the compound.* Much smaller peaks due to parent ion having less abundant isotopes may occur at masses one or two units higher but these are very easy to distinguish. The larger peaks at smaller masses correspond to the fragments produced by breakage of chemical bonds. Their location and their heights give clues to the nature of fragments produced as well as the relative strength of the different bonds in the molecule.

Let us now consider a simple example of mass spectrum analysis. Fig. 4.36 gives the mass spectrum of the compound called mercaptoethanol. The peak at the m/e value of 78 obviously corresponds to the molecular mass of the compound. The empirical formula of the compound C_2H_6OS must also be the molecular formula since the formula agrees with the molecular mass. If the structure had a $-CH_3$ group, there should have been a strong peak at the m/e value of 63. Since this is not the case, a $-CH_3$ group is ruled out. In the same manner, one can write a variety of structural formulae consistent with the molecular formula and compare each with the spectrum. It turns out that the formula $HSCH_2CH_2OH$ fits best with the observed spectrum.
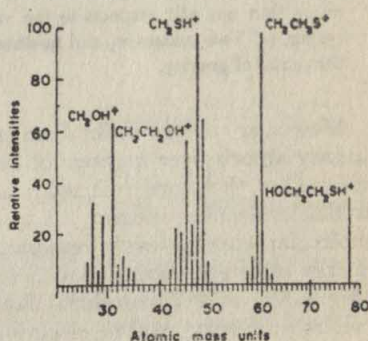
Fig. 4.36 Mass spectrum of mercapto-ethanol ($HSCH_2CH_2OH$)

We see that the mass spectrometric technique essentially involves writing down all conceivable structural formulae of the compound consistent with its empirical and molecular formulae and then choosing from them the formula which is most likely to yield the fragmentation pattern observed experimentally. This method has become a very powerful tool in recent years since precision instruments capable of measuring mass ratios within few parts per million† are now commercially available.

Only a milligram of sample is required to get a mass spectrum and the technique is equally applicable to large molecules. It is specially useful for organic compounds as it can easily distinguish several similar structures.

*Mass spectroscopy is the best method available today to determine exact molecular masses.
†The significance of this figure can be appreciated by noting that a modern instrument can easily distinguish between the following molecules

CO_2	44·0038	C_2H_4O	44·0403
CH_2NO	44·0277	C_2H_6N	44·0641
N_2O	44·0151	C_3H_8	44·0767

4.8.2 Molecular Spectroscopy

In spectroscopic methods, we employ electromagnetic radiation to determine the structure of a molecule.* Some concepts of spectroscopy were introduced earlier in Chapter 3 in connection with atomic spectra. Both absorption and emission spectra are given by molecules, but we shall limit our discussion only to the former. A molecule absorbs radiation of frequency ν (as in the case of atoms) if there are two energy levels spaced ΔE apart such that $\Delta E = h\nu$.
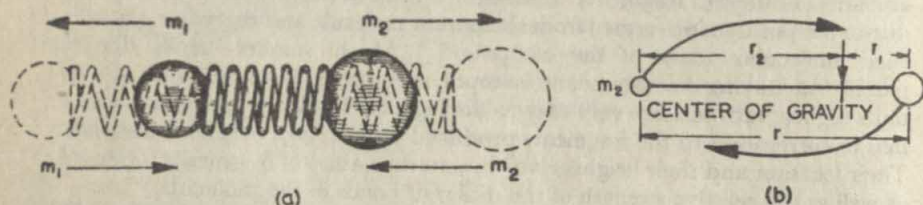
Fig. 4.37 (a) The vibrational motion of two atoms in a diatomic molecule is similar in many (but not all) respects to the vibrational motion of two masses connected by a spring. (b) Two masses m_1 and m_2 distance d apart undergoing rotational motion around the center of gravity.

Molecular spectra differ from *atomic spectra* (line spectra) in that molecules usually absorb over a range of frequencies known as absorption bands. Such spectra are, therefore, referred to as band spectra. A more important difference is that molecular spectra are of several kinds depending upon the type of molecular energy levels responsible for absorption. The different groups of energy levels are identified with (a) electronic motion, (b) vibrational motion (Fig. 4.37a), and (c) rotational motion (Fig. 4.37b) in a molecule. In a particular electronic energy level or electronic state of the molecule, a number of vibrational energy levels are available and each vibrational state possesses many rotational sublevels. This implies that electronic levels are most widely spaced (highest transition frequencies), followed by vibrational levels (medium transition frequencies), and then rotational levels (lowest transition frequencies). It is observed that typical frequencies for electronic absorption are in the ultraviolet and visible regions, for vibrational in the infrared and for

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*Some of the other methods using electromagnetic radiation are:

(i) The incident beam is scattered by the sample, the intensity of scattered radiation varying with angle in a manner depending upon the nature of the sample (x-ray diffraction). This is discussed in the next sub-section.

(ii) If the incident beam is plane polarised, the plane of polarisation is rotated by the sample (optical rotation).

(iii) If absorption takes place, its extent may depend upon the plane of polarisation (dichroism).

(iv) If scattering occurs, the scattered radiation may have the same frequency as the incident beam (Rayleigh scattering) or it may have different frequency (Raman scattering).

(v) The direction of the incident beam may be changed without changing the speed of the radiation (reflection) or with change of speed of radiation (refraction).

rotational in the far infrared and microwave regions. Chart 4.1 summarises this information.

Each kind of energy level in a molecule is characterised by a quantum number. The symbols n, v and J are usually used to denote the quantum numbers for the electronic, vibrational and rotational levels. As in the atomic case, selection rules exist which limit the possible transitions. While there is no restriction on changes in n, it can be shown that for absorption, only those vibrational and rotational transitions are permissible which satisfy the conditions

$$\Delta v = +1 \quad \text{and} \quad \Delta J = +1$$

Chart 4.1 Electromagnetic Spectrum and Spectral Transitions
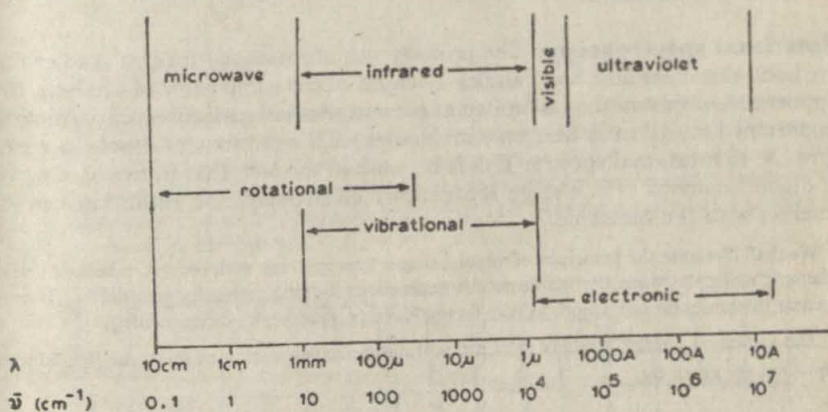
Molecular spectra are linked to structure because each type of energy levels (and hence the absorption frequencies) depend upon structural parameters like bond distance, bond angles and flexibility of a molecule. From a knowledge of the frequencies absorbed, it is possible to work out the details of molecular structure.

The instrument for observing and measuring different types of molecular spectra is called a *spectrometer*. Thus we have spectrometers covering the ultraviolet and visible regions of the spectrum, infrared spectrometers and microwave spectrometers. The construction of spectrometers varies according to the region of electromagnetic radiation used, but all spectrometers have four essential components. These are: (a) Source of radiation—this emits the electromagnetic radiation; invariably the emitted radiation contains a band of frequencies. (b) Monochromator or dispersing element which separates the bundle of frequencies into discrete units. (c) Sample cell that contains the sample under investigation on which falls the radiation from the monochromator. (d) Detector by which the radiation after traversing the cell is detected (or measured).

The exact form of these units differs according to the frequency range of the radiation used. Table 4.9 gives a summary of the principal components for different spectrometers.

The manner in which the absorption spectra are obtained and displayed is shown in Fig. 4.38. Here, the percentage transmission is plotted against frequency or wavelength. The wavelengths for which transmission is less than 100 per cent are obviously the ones which are absorbed.
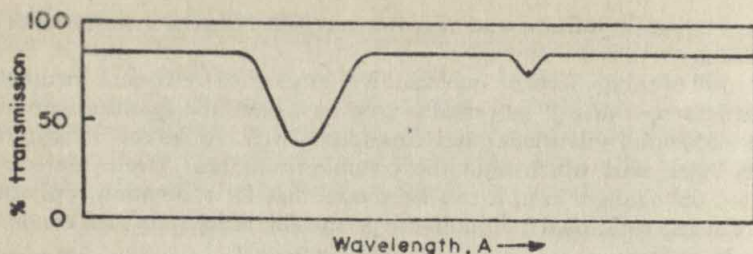
Fig. 4.38 A typical absorption spectrum. The minima correspond to the wavelengths absorbed by the sample.

Rotational spectroscopy: The primary use of rotational spectra is to evaluate bond distances and bond angles. Because of the complexity of analysis, the application of this method is limited at present to small molecules only. Another important limitation is that only molecules with a permanent dipole moment give rise to rotational spectra. This is because of the fact, that in the absence of a dipole moment (i.e. charge separation) electromagnetic radiation cannot interact with the molecule.

We shall illustrate the principles of rotational spectroscopy only with respect to heteronuclear diatomic molecules since the mathematical expressions for such molecules are simple. (Homonuclear diatomics do not absorb as they do not have permanent dipole moments.)

The rotational energy levels (E_J) of a diatomic molecule, computed from the Schrödinger equation, are given by,

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

where J is the rotational quantum number and I the moment of inertia defined below. The selection rule $\Delta J = +1$ for absorption means that the molecule can be excited to only the next higher rotational level (quantum number $J+1$). The energy gap (ΔE) between $J=0$ and $J=1$ is

$$\Delta E = E_{J=1} - E_{J=0}$$
$$= \frac{h^2}{8\pi^2 I} 1(1+1) - 0 = \frac{h^2}{4\pi^2 I}$$

It can be verified that the energy gap between any two successive levels is also given by the same expression, i.e. the rotational lines are equally spaced.

Table 4.9 Principal Components of Spectrometers

Type of spectrometer	Source	Dispersing element	Detector
Ultraviolet	H$_2$ discharge	Quartz prism or grating	Photomultiplier tube
Visible	Tungsten lamp	Glass prism or grating	Photomultiplier tube
Infrared	Heated ceramic element	Rock-salt prisms or grating	Thermocouple
Microwave	Klystron tube		Quartz crystal

From the Bohr frequency rule it follows that

$$h\nu = \Delta E = h^2/4\pi^2 I$$

or $\nu = h/4\pi^2 I$

or $\bar{\nu} = \nu/c = h/4\pi^2 Ic$

Now, the moment of inertia (I) is related to bond length (r) by

$$I = \mu r^2$$

where μ is called the reduced mass. If m_1 and m_2 are the masses of the two atoms then

$$\mu = m_1 m_2/m_1 + m_2$$

$$\bar{\nu} = \frac{h}{4\pi^2 c} \cdot \frac{1}{\mu r^2}$$

$$r = \sqrt{h/4\pi^2 c\mu}$$

$\bar{\nu}$ is measured from the experimental spectra and the rest of the quantities under the square root are known for a known molecule. Hence r can be calculated. (Here m_1 and m_2 are the masses of *individual* atoms. Since atomic masses are masses in grams of Avogadro number of atoms, m_1 and m_2 are the respective atomic masses in grams divided by the Avogadro number.) The rotational spectra for HCl molecule is shown in Fig. 4.39. Note the equal spacing between the lines as predicted by the theory.
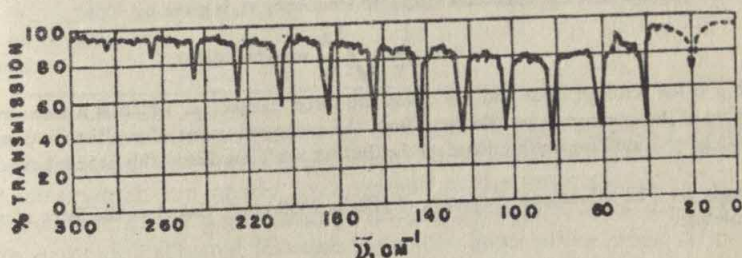
Fig. 4.39 The rotational spectrum of HCl. Note that the lines are equally spaced as demanded by the theory.

Example 4.3 Given that the spacing between the lines in the rotational spectra of HBr is 16·94 cm^{-1}, calculate the moment of inertia and bond length of the molecule.

$$\bar{\nu} = \nu/c = h/4\pi^2 cI$$

$$\therefore 16\cdot94 = h/4\pi^2 cI$$

$$\therefore I = \frac{h}{4\pi^2 c \times 16\cdot94} = 3\cdot303 \times 10^{-40} \text{ g.cm}^2$$

For HBr,

$$\mu = \frac{(1\cdot008)(79\cdot904)/(6\cdot02 \times 10^{23})^2}{(1\cdot008 + 79\cdot904)/(6\cdot02 \times 10^{23})}$$

$$= 1\cdot653 \times 10^{-24} \text{ g}$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{3\cdot303 \times 10^{-40} \text{ g.cm}^2}{1\cdot653 \times 10^{-24} \text{ g}}}$$

$$= \sqrt{\frac{3\cdot303}{1\cdot653}} \text{ cm}^2 \times 10^{-8}$$

$$= 1\cdot414 \times 10^{-8} \text{ cm} = 1\cdot414 \text{ A}$$

Vibrational spectroscopy: Molecules can execute a variety of vibrational motions (*vibrational modes*) involving stretching and contracting of bonds, bending and twisting of bond angles and so on. Each vibrational mode has a characteristic vibrational frequency. Unless there is a change in the dipole moment during one of the vibrations, the molecule does not absorb radiation. A diatomic molecule has only one possible vibrational mode—the symmetric stretching vibration of the bond. (A vibration is called symmetric if the symmetry of the molecule is preserved throughout the vibrational motion.) Thus amongst diatomics, only the heteronuclear types absorb in the infrared.

The vibrational energy levels (E_v) of a diatomic molecule are

$$E_v = (v+1/2)h\nu_m$$

where v is the vibrational quantum number and ν_m the vibrational frequency of the molecule. The energy levels are equally spaced with the energy gap (ΔE) between adjacent levels given by

$$\Delta E = h\nu_m$$

The frequency (ν) of radiation that can be absorbed is

$$\Delta E = h\nu = h\nu_m$$
$$\text{or} \qquad \nu = \nu_m$$

These are the only transitions permitted because of the selection rule $\Delta v = +1$.

It can be shown that the molecular vibration frequency ν_m is given by

$$\nu_m = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \nu \text{ (radiation)}$$

where μ is the reduced mass and k is called the force constant. k, which is a measure of the flexibility of the bond, can be calculated from the measured values of ν. Dissociation energy can also be obtained from vibrational spectra but we shall not discuss this aspect here.

Example 4.4 The vibrational frequency of HBr is 2559 cm^{-1}. Calculate the force constant of the molecule.

$$\bar{\nu} = 2559 \text{ cm}^{-1}$$
$$\bar{\nu} = 1/\lambda \text{ and } \nu\lambda = c$$
$$\therefore \nu = c/\lambda = c\bar{\nu}$$
$$= 3\cdot0 \times 10^{10} \times 2559$$
$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$
$$\text{or} \qquad \nu^2 = \frac{1}{4\pi^2} \frac{k}{\mu}$$
$$k = 4\pi^2 \mu\nu^2$$

Substituting the value of μ from Example 4.3, we get $k = 3\cdot846 \times 10^5$ dynes/cm.

The analysis of *vibrational spectra* of larger molecules is carried out by more elaborate methods, but the type of information obtained in these cases is essentially similar to that discussed above. In addition, symmetry and shapes of larger molecules can also be deduced from the nature of the vibrational spectra. Though strictly speaking, the force constant is related to the flexibility of a bond, it is observed in practice that it is a rough measure of the bond strength also. In Table 4.10 the force constant values for some bonds are shown. The relative values of triple, double and single bonded atoms correlate nicely with the strengths of these bonds.

Table 4.10 Force Constants of Some Bonds

Bond	Force constant (dynes/cm) × 10⁵	Bond	Force constant (dynes/cm) × 10⁵	Bond	Force constant (dynes/cm) × 10⁵
H—I	3·2	C—C	4·5–5·5	N=N	13·5
H—Br	4·1	C=C	9·5–9·9	N≡N	22·8
H—Cl	4·8	C≡C	15·6–17·0	C—O	5·0–6·0
H—F	9·7	N—N	4·0	C=O	12·0–13·5
C—H	5·0				

Table 4.11 Typical Vibrational Frequencies of Some Functional Groups

Bond	Approximate frequency (cm⁻¹)	Bond	Approximate frequency (cm⁻¹)	Bond	Approximate frequency (cm⁻¹)
O—H	3600	C—H (aliphatic)	2800–3000	C=O	1700–1750
N—H	3400	C≡N	2250	C—Cl	700–750
C—H (aromatic)	3050–3100				

A popular use of *infrared spectroscopy* depends upon the fortunate happening that specific bonds and chemical groups have characteristic infrared absorption frequencies which are nearly independent of the environment. Thus, it is found that the C—H group absorbs around 3000 cm⁻¹ while the OH group absorbs around 3600 cm⁻¹ in most molecules. Some other group frequencies are given in Table 4.11. More extensive tabulations exist which permit quick and easy identification of the functional groups in complex molecules. The great advantage of the infrared technique is that it can be used in the solid, liquid or gaseous state with as little as a milligram of the sample. The infrared spectrum is commonly referred to as the finger print of a molecule because no two molecules have exactly the same spectrum.

Electronic spectroscopy: Electrons in molecules occupy molecular orbitals of different energies giving rise to electronic energy levels. Transitions between these levels are induced by radiation in the visible or ultraviolet region. When an electron is excited from a lower to a higher molecular orbital, simultaneous changes in the vibration and/or rotational quantum numbers can take place. This means that absorption occurs over a range of energies and therefore, electronic spectra usually consist of broad absorption bands.

The position of the absorption bands of polyatomic molecules can be correlated with the type of bonds present. For example, conjugated molecules or molecules with double bonds or triple bonds (e.g. aromatic rings, carbonyl group, etc.) typically absorb in the 2000–6000 Å range. On the other hand, C—C, C—H and similar bonds absorb at less than 2200 Å. Thus, ultraviolet and visible spectra can also be used for identification of specific functional groups. Inorganic chemists extensively employ electronic spectra to characterise

transitions of transition metal ions in varying chemical environments. Electronic spectra can be obtained in any of the three states of aggregation.

Nuclear magnetic resonance spectroscopy: There are two other types of energy levels in molecular systems which are on a somewhat different footing from the above mentioned ones. These are associated with the nuclear spin and electron spin. They come into existence only when an external magnetic field is employed and the separation of energy depends upon the strength of the applied field. Thus the energy gap in these two cases can be controlled by the experimentalist while in the earlier cases it is fixed by the nature of the molecule. Transitions between these levels gives rise to *nuclear magnetic resonance* (NMR) spectra and *electron spin resonance* (ESR) spectra. We shall discuss only NMR as during the last twenty years, it has emerged as one of the most powerful and popular techniques to identify and analyse structure. The method depends on the fact that many nuclei like H^1 (proton) and F^{19} have intrinsic spin angular momenta and therefore, magnetic moments which interact with an external magnetic field giving rise to the nuclear spin energy levels. The maximum applications of the method have been to molecules containing proton nucleus (i.e. hydrogen atom). When molecules containing one or more hydrogen atom are placed in a magnetic field, the magnetic moment of the proton gets aligned. For a proton, quantum theory permits only two orientations which differ in energy; the energy separation being proportional to the strength of the magnetic field. In typical chemical experiments, this energy gap is so adjusted that 60 megacycle (6×10^7 cps) electromagnetic radiation is able to cause transitions between these energy levels. The utility of the magnetic resonance method arises from the fact that the local environment of a hydrogen atom in a molecule perturbs the energy gap slightly thus, modifying the frequency of absorbed radiation. Further, a specific type of chemical environment (e.g. hydrogen atom present as —OH or CH) produces a characteristic shift known as chemical shift. Thus, measurement of these shifts can yield information about the structure. Fig. 4.40 shows the spectrum of ethyl alcohol. NMR spectra, used widely in organic as well as in inorganic chemistry, are usually recorded of liquid samples.
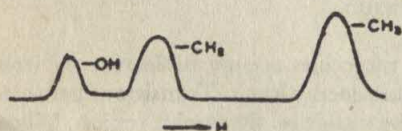
Fig. 4.40 The NMR spectrum of ethyl alcohol. There are three types of protons in the molecule so three different peaks are obtained. The —CH_2 peak is twice as intense as the —OH peak because there are two protons in the former and only one in the latter. Similarly the —CH_3 peak is thrice as intense as the —OH peak.

4.8.3 Diffraction Methods

The interference between waves, discussed in Chapter 3, underlies the diffraction methods for structure determination. There are three main methods in this category. The first is based on the wave nature of electromagnetic radiation in the x-ray region (x-ray diffraction) while the other two utilise the wave aspect of electrons and neutrons (electron diffraction and neutron diffraction). These techniques provide the values of bond distances and bond angles.

Since all radiation and all matter exhibit wave aspect, one may wonder why

only x-rays, electrons and neutrons are used for investigating molecular structure. The answer is based on the well-known principle that wave nature of an object becomes apparent only when it meets an obstacle of size comparable to the wavelength.*

Atomic size as well as interatomic spacing in molecules and crystals is typically of the order of few Angstroms; hence a wave of about 10^{-8} cm wavelength will show wave character in its interaction with molecules and crystals. X-rays and neutrons† (mass $\approx 10^{-24}$g) moving with velocity $\approx 10^8$cm/s all have wavelengths of about an Angstrom and therefore, they are used for molecular and crystal structure determination.

X-ray diffraction: Diffraction of x-rays by crystals is the most powerful method available at present for determination of crystal structure. This method also provides accurate structural parameters of molecules present in molecular crystals. To understand the mathematical requirement for interference, consider Fig. 4.41. In Fig. 4.41(a), two parallel x-ray waves, of wavelength λ, strike parallel lattice planes of a crystal. The dots in these planes denote either atoms (atomic crystals, e.g. diamond) or ions (ionic crystals, e.g. NaCl) or molecules (molecular crystal, e.g. naphthalene crystal). One of the waves is reflected by the surface plane of the crystal in such a way that the angle of reflection is equal to the angle of incidence. The second wave penetrates the crystal and is reflected by lattice plane immediately below the surface plane. It is obvious that if the two waves are in phase before reflection they will continue to be in phase after reflection provided the extra distance $(2d \sin \theta)$ that the second wave has to traverse is an integral multiple of the wavelength. In other words, the condition for constructive interference is

$$n\lambda = 2d \sin \theta \qquad (1)$$

where n is an integer and d the spacing between successive lattice planes. The above equation is referred to as the *Bragg condition* for diffraction in honour of W.L. and W.H. Bragg who pioneered the field of x-ray diffraction. In Fig. 4.41(b) we have two x-ray waves (again with wavelength λ) striking the same lattice planes as in (a) but at an angle θ' such that $2 \sin \theta' = \sin \theta$. If this is substituted in (1) we get

$$n\lambda/2 = 2d \sin \theta' \qquad (2)$$

which is the condition for (complete) destructive interference. This is because the additional distance that the second wave has to travel is an integral multiple of half the wavelength, in other words if the two waves are in phase before reflection, they will be exactly out of phase after reflection. It follows that if the intensity‡ (which is square of amplitude) of reflected x-ray radiation is measured in different directions, the intensity will vary from maximum along a direction where (1) is satisfied to minimum (or even zero) along a direction where (2) is satisfied.

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*This is the reason why visible light (wavelength $\approx 10^{-5}$cm) does not show wave characteristics in its interaction with macroscopic objects like a mirror.

†The wavelength of neutrons and electrons moving with known velocity is calculated from the de Broglie relation $\lambda = h/mv$ (see Chapter 3).

‡Intensity of reflected radiation is measured by means of an ionisation chamber which makes use of the fact that when x-rays pass through a gas, they ionise the moleculs. The motion of ionised molecules constitutes current and hence intensity can be obtained by measuring current.
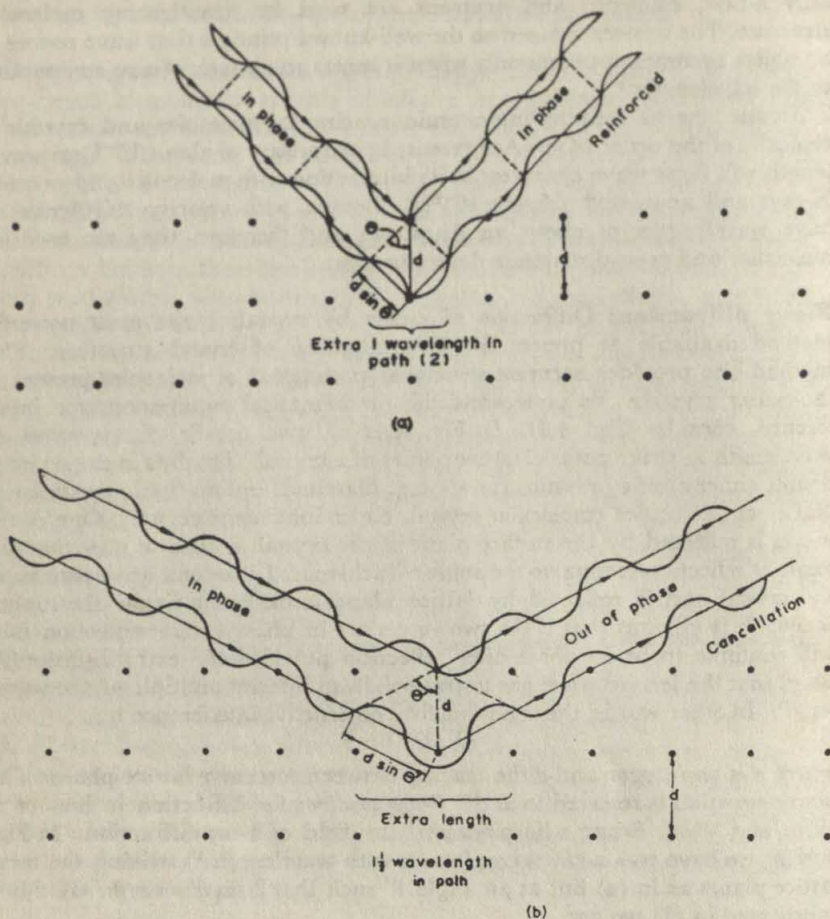
Fig. 4.41 The interference of x-rays. The dots define the lattice planes of a crystal. The horizontal planes are shown here to be separated by a distance d. In (a), the angle of incidence is such that the x-rays which are in phase continue to remain in phase after scattering. In (b), the angle of incidence is such that the x-rays after scattering are out of phase.

The experimental method consists of shining a monochromatic beam of x-rays at a known angle θ, on one of the faces of the crystal and rotating the crystal about an axis parallel to the face and perpendicular to the beam. See Fig. 4.42 for a schematic diagram of an *x-ray diffraction spectrometer*. For a particular face there will be a set of θ values which satisfy (1) and for which intensity will be maximum. These correspond to different values of n but it can be shown that the intensity decreases for increasing n. Hence it is possible to determine the value of n. The knowledge of n, λ and θ permits the evaluation of d, the distance between the lattice planes, which in turn yields the location of atoms (or ions or molecules) in the crystal. Further, since the electrons in these species are responsible for scattering of x-rays, the intensity of diffraction pattern is related to the number and distribution of the electrons at the lattice points.

From the analysis of the intensity pattern, it is possible to obtain electron density maps at the lattice sites. If the sites are occupied by molecules, bond lengths and bond angles (i.e. the shape of the molecule) can be accurately deduced from the electron density maps. If the sites are occupied by atoms and ions, then the intensity data reveal their ordering. In this way, it has been established that in the NaCl crystal, each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions.

One important limitation of the x-ray method is that it cannot locate hydrogen atoms precisely. This is because the hydrogen atom has only one electron and consequently it scatters x-rays very weakly. Another limitation is the time factor. Complete analysis of the diffraction pattern is a laborious process spanning several months, but the advent of high-speed computers is making this limitation less severe.

Fig. 4.42 A simplified view of x-ray diffraction sepectrometer. T is the tube in which x-rays are generated, L the collimator, C the crystal under investigation and P the photographic plate on which the scattered radiation strikes.

Electron diffraction: Electrons of wavelength around 10^{-8} cm are also scattered by atoms and molecules. Electrons striking an atom or a molecule are scattered by nuclei, unlike the x-rays which are scattered by the electrons in the atoms or molecules. Electron diffraction is primarily used to study samples in the gaseous phase. In a gas, molecules are tumbling in a random manner, and therefore, there is no fixed geometric relationship between neighbouring molecules but the atoms within a molecule are related by definite distances and definite angles. Hence electron diffraction pattern of gases provides information about molecular parameters and not lattice parameters. The mathematical condition for interference of electron waves is identical to 'hat derived for the x-rays. It is obvious that this method can be used only to study the structure of substances with high volatility. Also, because the analysis becomes complex for large molecules, the method is limited to analyse the structure of small molecules.

The apparatus consists of a chamber kept at relatively high vacuum. A heated filament provides the electrons which are then accelerated through a potential difference of about 40,000 volts. Under these conditions, electrons acquire a velocity which corresponds to about 1A wavelength. The sample to be studied is introduced in the diffraction chamber by means of a jet. Here, the electron beam interacts with the molecules of the sample and the scattered electrons fall on a photographic plate producing characteristic diffraction patterns. This technique also cannot locate hydrogen atoms precisely since the nucleus of hydrogen atom has low scattering power for electrons.

Neutron diffraction: The main advantage of neutron diffraction is that it locates hydrogen atoms easily because neutrons are scattered by the magnetic

Table 4.12 Comparison of Spectroscopic and of Diffraction Methods for Determination of Molecular Structures

Technique	Region	Time scale of		Form of sample	Remarks
		(a) experimental measurement	(b) analysis of results		
Mass spectrum		minutes/hours	minutes/hours	solid, liquid or gas	Very widely used
Spectroscopic methods					
Electronic	Ultraviolet/visible	minutes	minutes	solid, liquid or gas	'Finger-print' only, widely used
Vibrational (a) Infrared		minutes	minutes	solid, liquid or gas	'Finger-print' only, widely used
(b) Infrared Raman (visible)		minutes/hours	days/weeks	solid, liquid or gas	Full analyses only possible on small and/or highly symmetrical molecules
Rotational	Far infrared/Microwave	minutes/hours	days/weeks	gas	Very accurate moments of inertia for simple molecules
NMR	Radiowave	minutes	minutes/days	liquid	^1H, ^{19}F spectra, very widely used
Diffraction methods					
X-ray		hours/days	weeks	single crystal	A most powerful method; automatic instruments increase speed and usefulness
Neutron		hours/days	weeks	single crystal	Useful for locating protons more precisely
Electron		hours	days/weeks	gas	Extends the range covered by rotational spectroscopy

interaction with the nucleus and the magnetic moment of hydrogen atom nucleus is quite large. However, obtaining neutron beam of sufficient intensity is quite a problem and therefore this method is not as widely used as the x-ray and electron diffraction methods.

Table 4.12 summarises the highlights of the various spectroscopic and diffraction methods of determining molecular structures.

4.9 STRUCTURAL PARAMETERS OF MOLECULES

Bond distance: Experimental values of the bond distances show an interesting pattern. For example, it is found that

$$r_{HCl} \ (1 \cdot 36 \ A) = \tfrac{1}{2} r_{H_2} \ (0 \cdot 74 \ A) + \tfrac{1}{2} r_{Cl_2} \ (1 \cdot 98 \ A)$$

This relation is easily understood if we assume that atoms are like hard spheres and that they are in contact in a molecule. The bond distance is then just the separation between the centres of the two atoms or in other words, it is the sum of the radii of two atoms. Now, the formation of HCl from H_2 and Cl_2 can be pictured as shown in Fig. 4.43. In the first step, we imagine splitting of H_2 and Cl_2 into hydrogen and chlorine atoms and in the second step, we put together one hydrogen and one chlorine atom to give HCl. The hard sphere model means that the radius of the hydrogen atom will be one-half the bond distance of H_2. Similarly, the radius of the chlorine atom will be one-half the bond distance of Cl_2 and therefore the HCl bond distance should be the sum of the radii of the two atoms in agreement with the above observed relation. The radii of various atoms obtained from the observed bond lengths of diatomic molecules are given in Table 4.13.

This analysis implies that radii can be assigned to atoms and it should be possible to predict the bond lengths in molecules. However, the idea that an
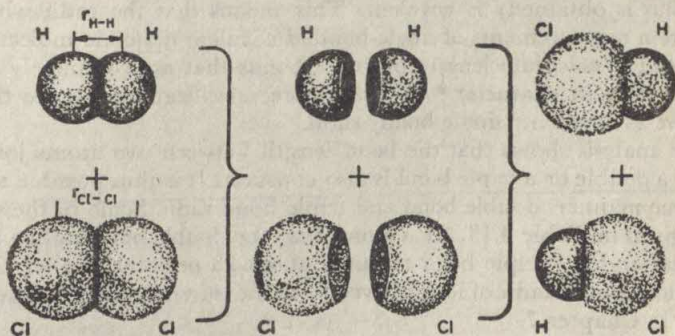
Fig. 4.43 An imaginary process showing formation of two HCl molecules from a H_2 and a Cl_2 molecule. On the left side are shown H_2 and Cl_2 molecules as two 'hard sphere' atoms in contact. The bond length of each molecule would be just twice the radii of respective atoms. In the middle, we imagine the break up of both the molecules into atoms. On the right, the hard sphere atom of hydrogen is joined to the hard sphere atom of chlorine resulting in HCl molecule. The bond distance of HCl is obviously the sum of radii of hydrogen atom and chlorine atom.

Table 4.13 Covalent Bond Radii

Single bond radii (A)						Multiple bond radii (A)
H	0·28	P	1·10	Te	1·37	C = 0·67
C	0·77	As	1·21	F	0·64	C ≡ 0·61
Si	1·17	Sb	1·41	Cl	0·99	N ≡ 0·55
Ge	1·22	O	0·66	Br	1·14	
Sn	1·40	S	1·04	I	1·33	
N	0·70	Se	1·17			

atom has a definite radius should be used with caution. The Schrodinger model of an atom shows that the atom is not a hard sphere. It does not even have a sharp boundary since electrons have different probabilities to be found at different distances from the nucleus. Therefore, it should not surprise us that bond lengths calculated from a fixed set of atomic radii do not always agree with the experimental values. For example, the C—C distance calculated from the carbon atom radius in Table 4.12 (obtained from C—C distance in diamond) should be 1·54 A. This agrees perfectly with the C—C distance measured in ethane, C_2H_6, but disagrees with the C—C distance in toluene, C_6H_5—CH_3 (1·51 A); the C—C bond in ethylene is still shorter (1·33 A). Similarly, the calculated C—F distance is 1·50 A, but the measured value in CF_4 is only 1·36 A. The reasons for these discrepancies are easy to understand. In ethylene, two sp^2 carbon atoms are linked by a double bond. In toluene the C—C bond of 1·51 A is between the sp^2 carbon of the aromatic ring and the sp^3 carbon of the CH_3 group unlike the C—C in C_2H_6 which is between two sp^3 carbons. In CF_4, the C—F bond is highly polar while the bond in F_2 (from which the fluorine atom radius is obtained) is covalent. This means that the radii which are derived from measurements of single-bonded covalent diatomic molecules can only be used to calculate lengths of single bonds that are completely or very nearly covalent in character.* We, therefore, specifically designate the radii used above as covalent (single bond) radii.

Similar analysis shows that the bond length between two atoms joined togethe. by a double or a triple bond is also constant. It is thus possible to assign in the same manner, double bond and triple bond radii. Some of these values are also given in Table 4.13. It is found that the double bond radius is about 14 per cent and the triple bond radius is about 23 per cent smaller than the single bond radius. Radii of ions derived form measurements in ionic solids are discussed in Chapter 7.

Bond energy: The energy required to break a bond is called the bond energy. For a diatomic molecule like H_2, the dissociation energy of the molecule is identical to the bond energy. For a polyatomic molecule like H_2O involving two bonds, the bond energy of the O—H bond is defined as one-half of the energy required to break H_2O into component atoms. Similarly, the N—H

---

*The C—C distance of toluene (1·51 A) is shorter than that of ethane because the former is not really a single bond but has appreciable double bond character.

bond energy in NH_3 is one-third of the energy required for the reaction

$$NH_3 \rightarrow N + 3H$$
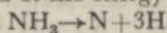
The type of analysis that we have used above for interpreting bond lengths can also be extended to bond energies. It may be argued that the contribution of each hydrogen atom to the bond energy of H_2 is one-half of the value of the bond energy. Similarly the contribution of an iodine atom will also be one-half of the bond energy of I_2. The bond energy of HI then should just be the sum of the hydrogen and iodine atom contribution. Let us test this idea. The experimental bond energies of H_2 and I_2 are respectively 104 kcal/mol and 36 kcal/mol. The calculated value of HI (E_{HI}) should then be

$$\epsilon_{H-I} = \tfrac{1}{2}\epsilon_{H-H} + \tfrac{1}{2}\epsilon_{I-I} = 70 \text{ kcal/mol}$$

This is in excellent agreement with the measured value of 71 kcal/mol.

The above procedure works only for molecules involving similar types of bonds. If we were to use the data obtained from singly-bonded covalent molecules to calculate the bond energies of highly polar bonds, we get poor results. In such cases, the empirical relation due to Pauling,

$$\epsilon_{A-B} = \tfrac{1}{2}\epsilon_{A-A} + \tfrac{1}{2}\epsilon_{B-B} + P(X_A - X_B)^2$$

works satisfactorily. In this equation, ϵ_{A-B}, ϵ_{A-A} and ϵ_{B-B} are the bond energies of the molecules $A-B$, $A-A$ and $B-B$ respectively, and X_A and X_B are the electronegativities of the atoms A and B, and P is a constant having dimensions of energy. If the bond energies are expressed in kcal/mol, then P has the value of equal to 23 kcal/mol.*

Table 4.14 gives the single-bond energies of some common bonds.

Table 4.14 Energies of Some Typical Bonds

Bond	Bond energy (kcal/mol)	Bond	Bond energy (kcal/mol)	Bond	Bond energy (kcal/mol)	Bond	Bond energy (kcal/mol)
F—F	38	O—F	44	C—F	116	H—O	111
Cl—Cl	58	C—O	85	N—Cl	48	N—H	93
Br—Br	46	H—F	135	C—Br	66	C—Cl	78
I—I	36	H—Cl	103	I—Cl	50	Si—I	51
H—H	104	H—I	71	C—H	99	P—Br	65
C—C	83			S—Cl	60		

Example 4.5 Calculate the bond energy of HCl.

From Pauling's equation,

$$\epsilon_{H-Cl} = \tfrac{1}{2}\epsilon_{H-H} + \tfrac{1}{2}\epsilon_{Cl-Cl} + 23(X_{Cl} - X_H)^2$$

Substituting the values from the tables,

$$\epsilon_{H-Cl} = 52 + 29 + 23(3{\cdot}0 - 2{\cdot}1)^2$$
$$= 52 + 29 + 18{\cdot}63 = 99{\cdot}63 \text{ kcal/mol}$$

This compares favourably with the experimental value of 103 kcal/mol. If we use the equation $\epsilon_{H-Cl} = \tfrac{1}{2}\epsilon_{H-H} + \tfrac{1}{2}\epsilon_{Cl-Cl}$, the value will be too low (81 kcal/mol).

*As stated in section 4.5.2, this relation was first used by Pauling to derive the electronegativity scale using the measured values of ϵ_{A-B}, ϵ_{A-A} and ϵ_{B-B}.

The relation given above can be interpreted in another way which is useful in the VB description. The term $23(X_A - X_B)^2$ may be viewed as the contribution to the bond energy of A—B due to the partial ionic character of the bond. The larger the difference in the electronegativities of the constituent atoms, the larger will be the ionic character and the stronger will be the bond. From the structural point, the fact that A—B has polar character means that (if $X_A > X_B$) A has greater attraction for the electron pair than B. If the molecule is highly polar, then the ionic structure is more important and if it is very weakly polar, the ionic structure will make insignificant contribution. For intermediate situations, the molecule may be regarded as a resonance hybrid of the covalent and the ionic structures and the extra stabilisation energy may be attributed to this ionic-covalent resonance. The term $23\ (X_A - X_B)^2$ is thus a direct measure of the resonance energy for the molecule A—B.

Example 4.6 Calculate the ionic resonance energy in the HF molecule.

The ionic resonance energy (Δ) is given by

$$\Delta = \epsilon_{A-B} - \tfrac{1}{2}\ (\epsilon_{A-A} + \epsilon_{B-B})$$

Therefore, for HF

$$\Delta = 135 - \tfrac{1}{2}(104 + 38) = 64 \text{ kcal/mol}.$$

4.10 RETROSPECTION

We discussed in this chapter the nature of bonding in isolated molecules. We have found three major types namely (a) the covalent type involving the sharing of an electron pair, (b) the polar covalent type in which the electron pair is unequally shared and (c) the ionic type in which an electron is transferred from one atom to another. In all these cases, bonding results from the interactions between electrons of different atoms comprising the molecule. As such, bonding in individual molecules is entirely due to intramolecular interactions. Chemists in general deal with not individual, but collections of molecules (of the order of 10^{23} molecules). In such collections, intermolecular interactions have also to be considered. These interactions are responsible for the formation of liquids and solids. If the intramolecular interactions are stronger than the intermolecular ones (as is generally the case), the molecules retain their identity even when they are clustered together in liquid or solid state; under such conditions, many properties of the collection can be understood in terms of the properties of the individual molecules. Liquids and solids for which this is valid are termed as molecular liquids and molecular solids. On the other hand, situations exist where it is meaningless to talk in terms of molecules or atoms. For example, in metals (like sodium) the entire collection of atoms is held together by a common pool of electrons and there are no molecules (like Na_2) or atoms (like Na) with electrons localised in the units. This type of bond, called the *metallic bond*, is discussed in Chapter 7. Similarly, in an ionic solid, like NaCl, there are no isolated pairs of Na^+—Cl^-, but the entire collection of the Na^+ ions and the Cl^- ions are held together by coulombic forces. This type of bonding existing in the solid state is an extension of the ionic bond discussed above and it is also dealt with in Chapter 7.

SUGGESTED READING

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PROBLEMS

4.1 What are the molecular species present in gaseous neon, hydrogen, bromine, krypton, and carbon dioxide?

4.2 (a) What do you understand by ' a molecular orbital ' (MO)?

(b) Give the maximum number of electrons that can occupy a MO.

(c) How many MOs of H_2 originate from the hydrogen $1s$ atomic orbitals?

(d) What is meant by bonding and anti-bonding MOs?

(e) Give the number of electrons which occupy the bonding MO in H_2^+, H_2, and He_2.

(f) Draw the bonding MO of H_2.

4.3 (a) Use the energy level diagram (Fig. 4.10) to show that N_2 would be expected to have a triple bond, F_2 a single bond and Ne_2 no bond. Suggest an appropriate electron configuration for C_2.

(b) What is the bond order of O_2^- and O_2^{2-} molecules?

4.4 Which of the following pairs of molecules would you expect to have the higher bond energy?

(a) F_2, F_2^+; (b) NO, NO^-; (c) BN, BO; (d) NF, NO; and (e) Be_2, Be_2^+.

4.5 Explain in terms of the MO theory the following observations: (a) the first ionisation energy of NO is less than that of CO; (b) the first ionisation energy of H_2 is greater than that of the H atom; and (c) the first ionisation energy of O_2 is less than that of the oxygen atom.

4.6 Which of the following pairs has greater electron affinity?

(a) OF and NF; (b) O_2^{2-} and N_2^{2-} or (c) CN and NO.

4.7 Explain in terms of the VB theory the following observations: (a) CCl_4 and $SiCl_4$ are both tetrahedral; (b) CO_2 is linear but SO_2 is angular; (c) HSH angle in H_2S is closer to $90°$ than the HOH angle in H_2O; (d) PCl_5 exists but not NCl_5 and (e) BF_3 is planar but NH_3 is not.

4.8 The valence electron configuration of Hg is $6s^2$. What kind of hybrid orbitals can be used to account for the linear geometry of $HgCl_2$?

4.9 Predict on the basis of the electron pair repulsion theory the geometry of the following molecule: (a) XeO_3, (b) XeO_4, (c) ClO_4^-, (d) PF_6^-, (e) $PbCl_2$, (f) CH_3^-, (carbanion), and (g) CH_3^+ (carbonium ion).

4.10 Compare and contrast the pure p-orbital model, the orbital hybridisation model and the valence electron-pair repulsion model for H_2O.

4.11 Construct the electron dot structure of (a) Cl_2, (b) HOCl, (c) BF_3, and (d) $SiCl_4$.

4.12 Write the resonance structure for (a) SO_2, (b) NO_2, (c) CO_3^{-2}, and (d) NO_3^-.

4.13 Account for the following order of dipole moments of the hydrogen halides: (a) HF (1·9D); (b) HCl (1·03 D); (c) HBr (0·74D); and (d) HI (0·38 D).

4.14 Calculate the energy of formation of ion pair Na^+Cl^- from gaseous atoms.

4.15 It is known from experiment that in gaseous ion pair of NaCl the equilibrium nuclear distance is 2·36 A. Calculate the potential energy of NaCl for this distance assuming point charge model.

4.16 The gaseous potassium chloride has a measured dipole moment of 10·0 D which indicates that it is a highly polar molecule. The separation between the nuclei in this molecule is $2·6 \times 10^{-8}$ cm. Calculate the dipole moment of a KCl molecule if there were opposite charges of one fundamental unit ($4·8 \times 10^{-10}$ esu) located at each nucleus. Calculate the percentage ionic character of KCl molecule.

4.17 Zero dipole moment of CCl_4 is consistent with tetrahedral structure. Which of the following conceivable structures for CCl_4 would also have a zero dipole moment: (a) Square planar, (b) square pyramid (carbon at the apex) and (c) irregular tetrahedron.

4.18 An absorption band with a maximum at 4900 A is observed for the Ti $(H_2O)_6^{3+}$ ion. Calculate the energy difference between the non-bonding orbital and the lowest antibonding orbital.

4.19 Predict the mass spectrum of ethyl alcohol.

4.20 Name the regions of the spectrum association with changes of (a) vibrational state, (b) rotational state, (c) nuclear spin state, and (d) electronic state.

4.21 (a) What is the relation between the energy of a rotational state of a linear molecule and the quantum number J? (b) To what accuracy can the bond lengths of small molecules be deduced from rotational spectra?

4.22 (a) Calculate the moment of inertia of a dumb-bell system in which two particles each of mass 1 gram are separated by a rigid rod 10 cm in length. (b) Calculate the moment of inertia of CO whose equilibrium bond length is 1·128 A.

4.23 In a measurement on the microwave spectrum of carbon monoxide ($^{12}C^{16}O$) the rotational line corresponding to the transition $J=0 \rightarrow 1$ is observed at 115,271·2 Megacycle per second (Mc/s). Calculate the internuclear distance in CO if the uncertainty in the frequency measurement is of the order of $\pm 0·1$ Mc/s. What is the estimated uncertainty in the bond distance determination? (It should be noted the uncertainty in frequency measurement is much less than we have quoted.)

4.24 It is a common practice to assume that the internuclear distances do no change on isotopic substitutions. Test the validity of the assumption by calculating the internuclear distances in HCl and DCl. Rotational line spacing in HCl is 20·68 cm^{-1} and in DCl is 10·65 cm^{-1}.

4.25 In the infrared spectrum of CH_3OH, the O—H stretching frequency occurs at 3300 cm^{-1}. Predict the frequency of the O—D bond in CH_3OD, assuming that the force constants of O—H and O—D bonds are the same.

4.26 A crystal when studied by the Bragg technique using x-rays of wavelength 2·29 A gave an x-ray reflection at an angle of 23° 20′. Calculate the corresponding interplaner spacing. With another x-ray source, the reflection was observed at 15° 26′. What was the wavelengh of the x-rays of the second source used?

5

Organic Molecules

...again the atoms gambolled before my eyes, but this time the small groups kept demurely in the background. My mind's eye sharpened by many previous experiences, distinguished larger structures of diverse forms: long series, closely joined together: all in motion, turning and twisting like serpents. But see what was that? One serpent had seized its own tail, and this image whirled defiantly before my eyes. As by a lightning flash I awoke: and again spent the rest of the night working out the consequences of this idea....
Let us learn to dream, gentlemen, and then we may find the truth but let us beware of making our dreams public before they have been approved by the waking mind.

A. VON KEKULE

In earlier chapters, we developed the principles underlying atomic and molecular structure and nature of the chemical bond. In this chapter we shall apply these principles, as far as possible, to discuss the different types of organic compounds and the isomerism in these compounds.

5.1 TYPES OF ORGANIC COMPOUNDS

Organic chemistry is the chemistry of carbon compounds. The number of carbon compounds known today far exceeds the number of compounds formed from all the other 105 elements of the periodic table. This feature of carbon chemistry may be attributed to the high covalency of carbon which permits a large number of groups to be attached to it in a variety of ways. In addition, the relatively high strength of the C—C bond enables the formation of chains of carbon compounds of unlimited length. The ability of carbon to form multiple bonds with itself and other elements also contributes to the variety. It might be pointed out here that the unusual ability of carbon to form compounds containing large number of carbon–carbon single and multiple bonds is not exhibited by even closely related elements like silicon and germanium. Compounds of silicon containing more than eight silicon atoms in a row are not yet known. In contrast to the numerous compounds containing carbon–carbon multiple bonds, no compound of silicon is known in which a silicon atom is involved in multiple bond formation.

In this section we shall examine some of the types of organic compounds which are of common occurrence and use.

5.1.1 Hydrocarbons

Organic compounds containing carbon and hydrogen are referred to as *hydrocarbons*. They can be grouped under three major classes, (*i*) acyclic hydrocarbons, (*ii*) alicyclic hydrocarbons and (*iii*) aromatic hydrocarbons.

Acyclic hydrocarbons: In these, the carbon atoms are bonded together in the form of chains (linear or branched) and they can be of three different types: (*a*) alkanes, which are acyclic hydrocarbons, containing carbon–carbon single bonds, (*b*) alkenes, which contain carbon–carbon double bonds and (*c*) alkynes, which contain carbon–carbon triple bonds.

Alkanes: The simplest alkane, methane CH_4, is the chief constituent of natural gas. A complex mixture of various hydrocarbons and certain other compounds containing O,N,S and small amounts of other elements are present in petroleum which perhaps is the most abundant natural source for these hydrocarbons. Alkanes have the general formula C_nH_{2n+2} and they are referred to as saturated hydrocarbons or *paraffins*. The names and structures of some of the simpler hydrocarbons are shown in Table 5.1. Hydrocarbons in which all the carbon atoms are joined together in a continuous chain are known as normal, linear, or continuous chain hydrocarbons. On the other hand, if the carbon chain is branched, then the alkanes are called branched chain hydrocarbons (e.g. *iso*-butane, *iso*-pentane, etc.).

The first four members are known by their common (non-systematic) names, methane, ethane, propane and butane. The higher members—from pentane onwards—have names beginning with a numerical prefix (pent-, hex-, hept-, etc., denote the number of carbon atoms in the molecule) and ending with 'ane'. A series, like alkanes, in which successive members differ from one another by a CH_2 group, is known as a *homologous series*. The names of some of the normal alkanes and their molecular formulae are given in Table 5.2.

Table 5.1 Structures of Some Simple Alkanes

Name	*Molecular formula*	*Structure*	*Name*	*Molecular formula*	*Structure*
Methane	CH_4	$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$	*Iso*-Butane	C_4H_{10}	$CH_3-CH-CH_3$ $\quad\;\; \mid$ $\quad\;\; CH_3$
Ethane	C_2H_6	CH_3-CH_3	*n*-Pentane[1]	C_5H_{12}	$CH_3-(CH_2)_3-CH_3$
Propane	C_3H_8	$CH_3-CH_2-CH_3$	*Iso*-Pentane	C_5H_{12}	$CH_3-CH-CH_2-CH_3$ $\quad\;\; \mid$ $\quad\;\; CH_3$
n-Butane[1]	C_4H_{10}	$CH_3-CH_2-CH_2-CH_3$	*Neo*-Pentane	C_5H_{12}	$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$

[1]The prefix *n* denotes the normal straight chain structure.

Table 5.2 Names and Molecular Formulae of Some Normal Alkanes

Number of carbon atoms	Name	Molecular formula[1]	Number of carbon atoms	Name	Molecular formula[1]
4	n-Butane	C_4H_{10}	8	n-Octane	C_8H_{18}
5	n-Pentane	C_5H_{12}	9	n-Nonane	C_9H_{20}
6	n-Hexane	C_6H_{14}	10	n-Decane	$C_{10}H_{22}$
7	n-Heptane	C_7H_{16}			

[1]From butane onwards, each alkane has several *isomers*, the number of isomers increasing with the number of carbon atoms. *Isomerism* means two or more molecules having same molecular formula but different structural arrangement. See section 5.2.1 for further details.

Alkyl groups derived from alkanes by removal of one of the hydrogen atoms are named by replacing the ending 'ane' of the hydrocarbon by the ending 'yl' (e.g. meth*ane*——→meth*yl*). Some examples are shown below:

CH₃—   CH₃—CH₂—CH₂—   CH₃—CH₂—CH₂—CH₂—

Methyl   n-Propyl   n-Butyl

CH₃—CH₂—   H₃C⟩CH—   H₃C⟩CH—CH₂—

Ethyl   Isopropyl   Isobutyl

CH₃—C(CH₃)(CH₃)—   CH₃—C(CH₃)(CH₃)—CH₂—   CH₃—CH—CH₂—CH₃

tert-Butyl   Neopentyl   sec-Butyl
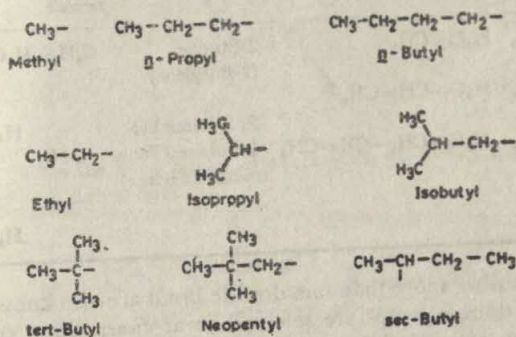
Bonding in acyclic alkanes: In the simplest of acyclic alkanes, namely methane, we know on the basis of experimental evidence, that all the C—H bonds are equivalent and that the H—C—H bond angle is 109·5°. These facts can be accounted in terms of a tetrahedral model in which the carbon atom occupies the centre of a regular tetrahedron and the four hydrogen atoms the four corners (Fig. 5.1). As discussed in Chapter 4, the shape and bonding in methane can be explained in terms of hybridised orbitals. Each C—H bond in methane is formed by the overlap of an sp^3 orbital of carbon with the 1s orbital of hydrogen and the bond is of the sigma(σ) type (Fig. 5.1).
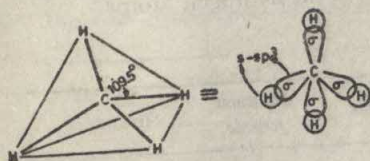
Fig. 5.1 Bonding in methane   **Fig. 5.2** Bonding in ethane
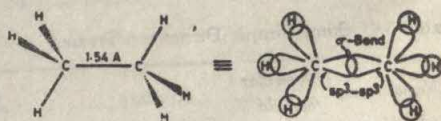
Unlike methane, the other saturated hydrocarbons such as ethane, or propane (Table 5.1) have both C—H and C—C bonds in their molecules. The C—C bonds in these compounds are formed by the overlap of sp^3 orbitals

of two carbon atoms, whereas the C—H bonds are formed by the overlap of the sp^3 orbitals of carbon with the $1s$ hydrogen orbital. The bonding in ethane is indicated in Fig. 5.2.

Alkenes: Alkenes are unsaturated hydrocarbons containing one carbon–carbon double bond and have the general formula C_nH_{2n}. They can be treated as derived from alkanes by the loss of two hydrogen atoms from adjacent carbons and they are commonly referred to as unsaturated hydrocarbons or *olefins*. Some of the representative examples of alkenes are listed in Table 5.3.

Alkenes having one double bond are named by the replacement of the ending ' ane ' (used in alkanes) by ' ene '. The non-systematic names of the simplest members such as ethylene, propylene and butylene are also commonly used in naming these compounds.

Table 5.3   Some simple Alkenes and their Structures

Name	Molecular formula	Structure	Name	Molecular formula	Structure
Ethene (Ethylene)	C_2H_4	$H_2C=CH_2$	2-Butene (2-Butylene)	C_4H_8	$H_3C—CH=CH—CH$
Propene (Propylene)	C_3H_6	$H_3C—CH=CH_2$	2, 3-Dimethyl-2-butene (Tetra-methylethylene)	C_6H_{12}	
1-Butene (1-Butylene)	C_4H_8	$H_3C—CH_2—CH=CH_2$			

$$\begin{array}{ccc} H_3C & & CH_3 \\ \diagdown & & \diagup \\ & C=C & \\ \diagup & & \diagdown \\ H_3C & & CH_3 \end{array}$$

Alkenes containing more than one double bond are also known. Compounds containing two double bonds are referred to as *dienes*, those containing three double bonds as *trienes* and those containing many double bonds as *polyenes*. Examples of dienes and trienes are listed in Table 5.4. Molecules, like polyenes, which contain a sequence of alternate single and double bonds are said to exhibit *conjugation*. As conjugation increases, the wavelength of the radiation absorbed by the molecules also increases. Consequently, whereas smaller polyenes absorb in the ultraviolet (i.e. they are colourless), the larger ones absorb in the visible region (i.e. they are coloured). The polyenes present in carrots, tomatoes, etc., are commonly referred to as *carotenes* and they are responsible for the colour of these vegetables.

Alkenyl groups, like alkyl groups, can be regarded as derived from the corresponding alkenes by the removal of one of the hydrogen atoms.

Table 5.4   Some Simple Dienes and Trienes

Name	Molecular formula	Structure	Name	Molecular formula	Structure
Propadiene (Allene)	C_3H_4	$H_2C=C=CH_2$	2-Methyl-1,3-butadiene (Isoprene)	C_5H_8	$H_2C=C—CH=CH_2$ $\mid$ CH_3
1,3-Butadiene	C_4H_6	$H_2C=CH—CH=CH_2$			
1,3,5-Hexa-triene	C_6H_8	$H_2C=CH—CH=CH—CH=CH_2$			

Some of the common alkenyl groups are listed below:

$CH_2=CH-$ $CH_2=CH-CH_2-$ $CH_3-CH=CH-$ $CH_3-CH=CH-CH_2-$
Vinyl   Allyl   Propenyl   Crotyl
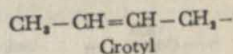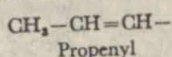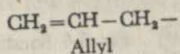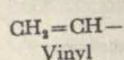
Bonding in ethylenic compounds: The bonding in ethylene and similar unsaturated compounds is characterised by the presence of a carbon–carbon double bond. In ethylene, for example, each of the carbon atoms is attached to two hydrogen atoms by a single bond and the two carbon atoms are joined together by a double bond. The carbon atoms are trigonally (sp^2) hybridised and they are held together by a σ bond, (formed by the overlap of two sp^2 orbitals) and a π bond (due to the overlap of two p orbitals). Each of the C—H bonds is formed as a result of the overlap of an sp^2 hybrid obital of carbon with the $1s$ orbital of hydrogen (Fig. 5.3.). The properties of ethylene are in agreement with such a representation.

Fig. 5.3 Bonding in ethylene
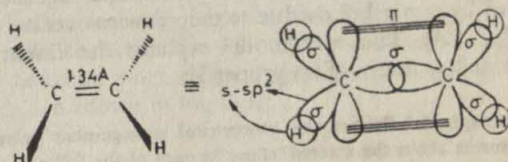
Example 5.1 Sketch the $\sigma-\pi$ model of allene ($CH_2=C=CH_2$) and indicate the state of hybridisation of each carbon atom.
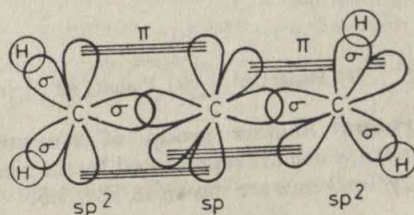
Alkynes: Unsaturated acyclic hydrocarbons having one or more carbon–carbon triple bonds are called alkynes. The simplest member of the series is acetylene, C_2H_2. The common method of naming these compounds is to employ the ending 'yne' in place of 'ane' used for the naming of the saturated hydrocarbons. Some representative examples are listed in Table 5.5.

Table 5.5 Some Simple Alkynes and their Structures

Name	Molecular formula	Structure	Name	Molecular formula	Structure
Ethyne (Acetylene)	C_2H_2	$H-C\equiv C-H$	2-Butyne (Dimethyl-acetylene)	C_4H_6	$H_3C-C\equiv C-CH_3$
Propyne (Methylacety-lene)	C_3H_4	$H_3C-C\equiv C-H$	1,3-Buta-diyne	C_4H_2	$H-C\equiv C-C\equiv C-H$

$$H.-C \equiv C-H \quad \equiv$$
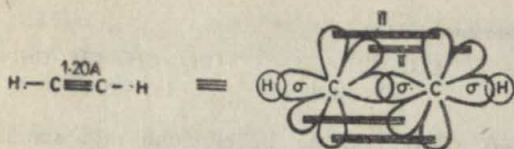
Fig. 5.4 Bonding in acetylene

Several polyacetylenes occur in nature as constituents of plants and a few of these have been recently isolated. The common alkynyl groups are ethynyl ($H-C \equiv C$) and propargyl ($H-C \equiv C-CH_2-$) groups.

Bonding in acetylenic compounds: In acetylene, C_2H_2, we have the example of an unsaturated hydrocarbon containing a carbon–carbon triple bond. The four atoms of acetylene are linear and the H—C—C angle is $180°$. The carbon atoms of acetylene are *sp* hybridised (Chapter 4) and the C—H bonds are formed by the overlap of the *sp* hybrid orbitals with *s* orbitals of hydrogen. The two carbon atoms are held together by one σ bond (*sp–sp* overlap) and by two π bonds due to the sidewise overlap of the unhybridised *p* orbitals (Fig. 5.4). This σ–π model explains the linear shape of acetylene molecule as well as many of its properties.

Example 5.2 Predict the geometrical arrangement (tetrahedral, planar, linear, etc.) of sub-stituents about the starred atoms in each of the following molecules and indicate the type of hybridisation.

    (a) $\overset{*}{C}HCl_3$ (b) $\overset{*}{C}H_2=CH-CH=CH_2$ (c) $Cl_2\overset{*}{C}=CCl_2$

    (d) $Cl-\overset{*}{C}\equiv C-Cl$
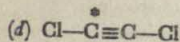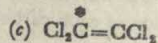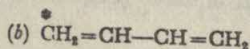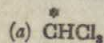
    (a) Tetrahedral; sp^3 (b) Planar; sp^2 (c) Planar; sp^2 (d) Linear; sp

Alicyclic hydrocarbons: Another group of saturated hydrocarbons is made up of cycloalkanes which are represented by the general formula C_nH_{2n}. Examples of simple cycloalkanes are shown in Fig. 5.5.

Cyclopropane   Cyclobutane   Cyclopentane   Cyclohexane
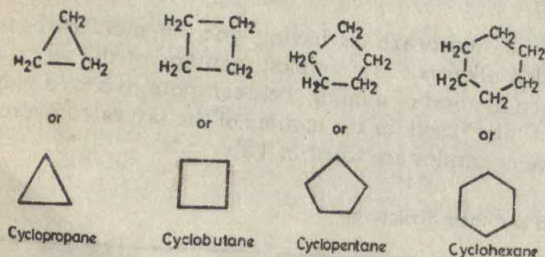
Fig. 5.5 Some simple cycloalkanes
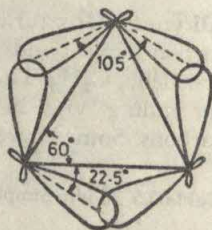
Fig. 5.6 Bent bonds in cyclopropane

The simplest member of the cycloalkane series is cyclopropane. It is observed that this hydrocarbon is more reactive than the analogous saturated hydro-carbon, a fact attributed to its distinctive structure. It is now known that the bonding in cyclopropane involves bent bonds as indicated in Fig. 5.6.

The incorporation of carbon–carbon double bonds and carbon–carbon triple bonds in a cyclic system gives rise to cycloalkenes and cycloalkynes,

respectively. Cycloalkynes containing less than seven carbon atoms have not been prepared. A few examples of cycloalkenes and cycloalkynes are shown in Fig. 5.7.

Cyclopentene   Cyclohexene   Cycloheptyne   Cyclooctyne
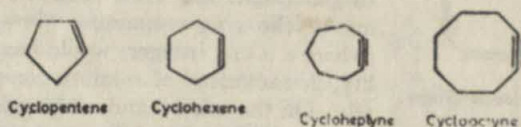
Fig. 5.7 Some cycloalkenes and cycloalkynes

Aromatic hydrocarbons: Benzene is the parent member of a very large number of organic compounds which contain unsaturated ring systems as part of their structural make-up. Since many substances of this group display characteristic, often pleasant odour, benzenoid compounds were collectively referred to as ' *aromatic* '—a term still commonly used.

There are a large number of organic compounds which exhibit properties similar to those of benzene (*aromatic character*). They are either substituted benzenes or contain two or more benzene rings. Some representative examples of different aromatic compounds are shown in Fig. 5.8.

Toluene   o-Xylene   m-Xylene   p-Xylene
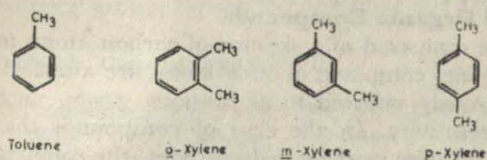
Fig. 5.8 Some aromatic hydrocarbons

Biphenyl   Naphthalene   Anthracene

The common aryl groups derived from benzene, toluene and naphthalene are indicated below:

Phenyl   Benzyl   o-Tolyl   m-Tolyl   p-Tolyl   ∝-Naphthyl   β-Naphthyl
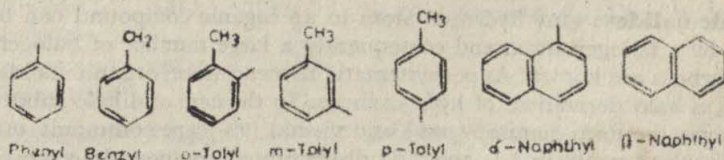
Bonding in aromatic hydrocarbons: The bonding in benzene is representative of other aromatic hydrocarbons. Benzene is a symmetrical molecule in which all carbon and hydrogen atoms lie in the same plane with H—C—C and C—C—C bond angles of 120°. As mentioned in Chapter 4, each of the carbon atoms in benzene is sp^2 hybridised and the p orbitals can overlap with both neighbours. This results in two continuous hexagonal electron clouds; one lying above and the other below the plane containing carbon and hydrogen atoms (Fig. 5.9).
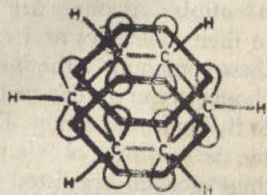
Fig. 5.9 Atomic orbital model of benzene

13

The characteristic feature of the bonding in benzene and other aromatic hydrocarbons is the delocalisation of π electrons. In general, it has been observed that a planar monocyclic ring containing $(4n+2)$ π electrons (where n is any integer) would have special stability, characteristic of aromatic compounds (*Hückel rule*). On the other hand, ring systems containing $(4n)\pi$ electrons will not show any additional stability and such systems are referred to as *anti-aromatic* compounds. Cyclobutadiene and cyclooctatetraene are examples of anti-aromatic compounds.
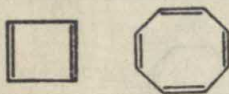
Cyclobutadiene   Cyclooctatetraene

Example 5.3 Write the structural formulae for the following compounds: (*a*) *Iso*-pentane, (*b*) *Iso*-butene, (*c*) 3-Methyl-1-butene, (*d*) Vinylacetylene, and (*e*) *sec*-Butylbenzene.

(a) $\underset{CH_3}{\overset{CH_3}{>}}CH-CH_2-CH_3$ (b) $\underset{CH_3}{\overset{CH_3}{>}}C=CH_2$.

                                                   (e) $CH_3-CH-CH_2-CH_3$

(c) $CH_3-\underset{CH_3}{\overset{|}{C}H}-CH=CH_2$ (d) $CH_2=CH-C\equiv CH$
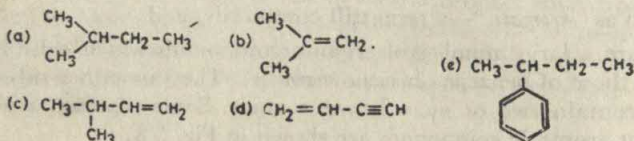
5.1.2 Functionally Substituted Organic Compounds

In general, organic molecules are composed of a skeleton of carbon atoms to which hydrogen atoms and groupings composed of other atoms are attached. These attached groups are commonly referred to as *functional groups*, since they are the sites of chemical reactivity. In the class of compounds that we have discussed earlier in this chapter, namely hydrocarbons, the common functional groups are the π part of double and triple bonds of the unsaturated hydrocarbons. The lesser reactive C—C and C—H σ bonds are not commonly referred to as functional groups. Most of the functional groups in organic molecules, however, are generated from heteroatoms (halogens, O, N, S, P, etc.). In this section, we shall examine few representative examples of the various functionally substituted organic compounds.

Organic halides: Any hydrogen atom in an organic compound can be replaced by a halogen atom and consequently a large number of halogenated hydrocarbons are known. As per systematic nomenclature, organic halides are named as halo derivatives of hydrocarbons. In the case of dihalo substituted derivatives, the term geminal (*gem-*) and vicinal (*vic-*) are commonly used to indicate substitutents in 1,1- and 1,2- disubstituted compounds respectively.

The names and structures of common organic halides are listed in Table 5.6.

Alcohols: Alcohols are characterised by the presence of a hydroxyl group in their molecules and can be considered as derivatives of water. In naming these compounds, the largest chain to which the hydroxyl group is attached is chosen as the parent structure and the chain is numbered from the end closest to the hydroxyl group. The ending ' e ' of the name of hydrocarbon is replaced by the ending ' ol ' (e.g. Ethan*e* → Ethan*ol*). The names and structures of some alcohols are listed in Fig. 5.10.

Alcohols can be regarded as derivatives of water formed by the replacement of one of the hydrogen atoms by alkyl groups. In the case of methanol, for example, the carbon–oxygen σ bond is through the overlap of one of the sp^3
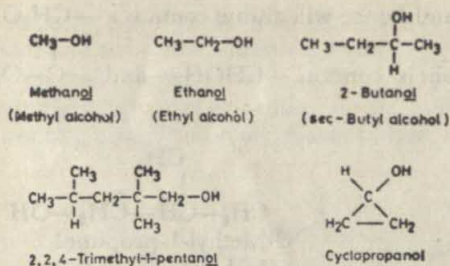
Fig. 5.10 Examples of alcohols
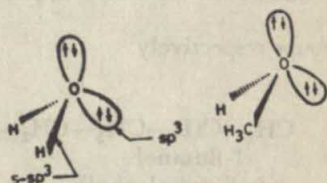
Fig. 5.11 Water and methanol

hybrid orbital of carbon (of the methyl group) with an sp^3 hybrid orbital of oxygen. The O—H bond, on the other hand, is due to the overlap of the $1s$ orbital of hydrogen with the sp^3 hybrid orbital of oxygen. The shape of methanol (Fig. 5.11) resembles that of water and the C—O—H angle is close to the tetrahedral angle.

Alcohols are commonly designated as *primary*, *secondary* and *tertiary* depending on the number of carbon atoms directly attached to the carbon bearing the hydroxyl group. *Primary* alcohols have one alkyl group attached to the carbon

Table 5.6 Common Organic Halides

Name	Molecular formula	Structure	Name	Molecular formula	Structure
Methyl chloride (Chloromethane)	CH_3Cl		Chlorobenzene	C_6H_5Cl	
Methyl bromide (Bromomethane)	CH_3Br		o-Dichlorobenzene	$C_6H_4Cl_2$	
Methyl iodide (Iodomethnae)	CH_3I		m-Dichlorobenzene	$C_6H_4Cl_2$	
Methylene chloride (Dichloromethane)	CH_2Cl_2				
Freon (Dichlorodi-fluoro methane)	CCl_2F_2		p-Dichlorobenzene	$C_6H_4Cl_2$	
Chloroform (Trichloromethane)	$CHCl_3$		Gammexane (Benzene hexachloride)	$C_6H_6Cl_6$	
Carbon tetrachloride (Tetrachloromethane)	CCl_4				
Trichloroethylene	C_2HCl_3		1-Bromonaphthalene	$C_{10}H_7Br$	
			2-Bromonaphthalene	$C_{10}H_7Br$	

atom bearing the hydroxyl group and hence will always contain a —CH$_2$OH

grouping; *secondary* and *tertiary* alcohols contain —CHOH— and —C—OH

groups respectively.

CH$_3$—CH$_2$—CH$_2$—CH$_2$—OH
1-Butanol
(*n*-Butyl alcohol)
(*Primary* alcohol)

$$CH_3$$
$$CH_3—CH—CH_2—OH$$
2-Methyl-1-propanol
(*Iso*-butyl alcohol)
(*Primary* alcohol)
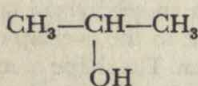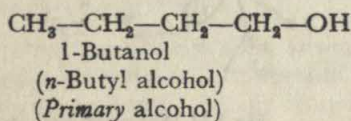
CH$_3$—CH—CH$_3$
    |
    OH
2-Propanol
(*Iso*propyl alcohol)
(*Secondary* alcohol)
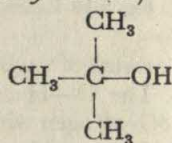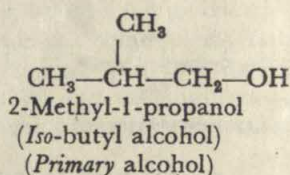
$$CH_3$$
$$CH_3—C—OH$$
$$CH_3$$
2-Methyl-2-propanol
(*tert*-Butyl alcohol)
(*Tertiary* alcohol)

The simplest members of alcohols such as methanol, ethanol, and propanol are soluble in water and their physical and chemical properties resemble those of water to a considerable extent. For example, the boiling points of alcohols are abnormally high as compared to the boiling points of hydrocarbons, ethers and related substances having nearly the same molecular masses. The higher boiling points of alcohols are attributed to hydrogen bonding as in the case of water.

When a hydroxyl group is attached to an aromatic ring, the compound is referred to as a *phenol*. Some of the common phenols are listed in Fig. 5.12.

Phenol
(Hydroxybenzene)

α - Naphthol
(1-Hydroxynaphthalene)

β - Naphthol
(2-Hydroxynaphthalene)

Catechol
(o-Dihydroxybenzene)

Resorcinol
(m-Dihydroxybenzene)

Hydroquinone
(p-Dihydroxybenzene)

Phloroglucinol
(1, 3, 5 - Trihydroxybenzene)

p - Bromophenol
(4-Bromohydroxybenzene)
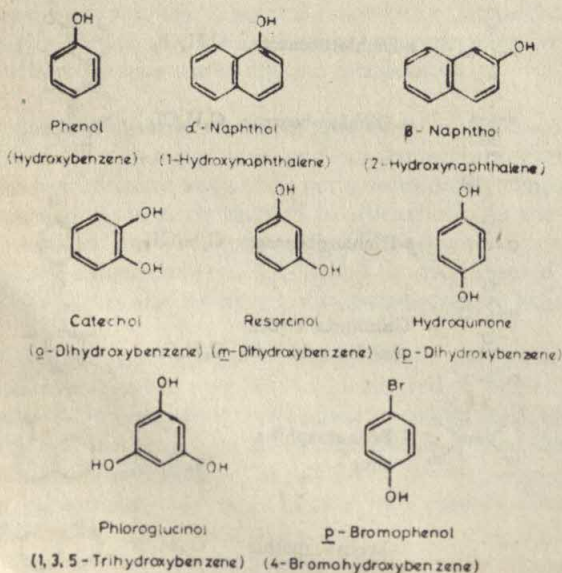
Fig. 5.12 Common phenols

As compared to alcohols, phenols are either high boiling or high melting solids and are commercially obtained from coal tar fractions. Phenols, in general, are more acidic than alcohols, a feature that is understood in terms of the greater stability of the phenoxide ion due to resonance. Some of the resonance structures of phenoxide ion are shown below:
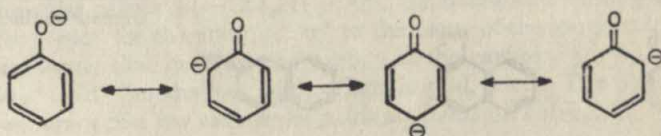
Ethers: Ethers can be regarded as derivatives of water with the successive replacement of the hydrogen atoms by hydrocarbon groups. They are used as common solvents for organic compounds. Some examples of the common ethers are listed in Fig. 5.13. Several ethers occur in nature and some of them, such as *vanillin* (responsible for flavour of vanilla), are of commercial importance.

$$CH_3-O-CH_3 \qquad CH_3-O-CH_2-CH_3$$

Dimethyl ether   Methyl ethyl ether
(Methoxymethane)   (Methoxyethane)
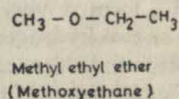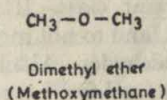
Fig. 5.13 Examples of common ethers

$$CH_3-CH_2-O-CH_2-CH_3 \qquad CH_3-O-C_6H_5$$

Diethyl ether   Methyl phenyl ether
(Ethoxyethane)   (Anisole)

$$C_6H_5-O-C_6H_5$$
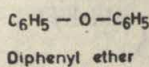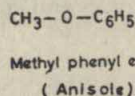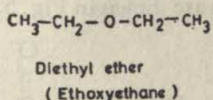
Diphenyl ether   Tetrahydrofuran   Dioxane   Vanillin
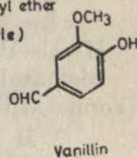
Amines and related compounds: Organic amines can be regarded as derivatives of ammonia. They are commonly named by indicating the hydrocarbon groups attached to the nitrogen and adding the word 'amine' as ending. They are named systematically as the amine derivatives of hydrocarbons. Amines are classified as *primary*, *secondary* and *tertiary* depending on the number of groups attached to the nitrogen atom. Thus, methylamine is a *primary* amine; methylethylamine, a *secondary* amine; and triethylamine, a *tertiary* amine.

$$CH_3-NH_2 \qquad CH_3-\overset{\overset{\text{H}}{|}}{N}-CH_2-CH_3 \qquad (CH_3-CH_2)_3N$$

Methylamine   Methylethylamine   Triethylamine
(Aminomethane)   (N-methylaminoethane)   (N, N-Diethylaminoethane)
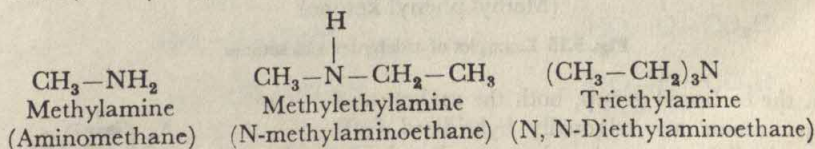
The common name for the parent aromatic amine is aniline. Some simple aromatic amines are listed in Fig. 5.14.

Amines resemble ammonia in their basic character and also their ability to form salts with acids. The salts derived from amines are referred to as *quaternary ammonium compounds*.

Aniline   o-Toludine   m-Nitroaniline   N-Methylaniline
(Aminobenzene)
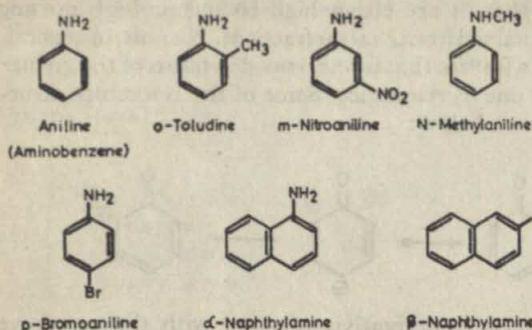
Fig. 5.14 Examples of aromatic amines

p-Bromoaniline   ⍺-Naphthylamine   β-Naphthylamine

In nature, amines are widely distributed as amino acids, proteins and alkaloids. Some of these substances are the primary building blocks of animal tissues and they are discussed in detail in Chapter 18.

Aldehydes and ketones: Organic compounds containing the *carbonyl group*, $>C=O$, form a very important class. If the carbonyl carbon is bonded to one or two hydrogen atoms (and to not more than one alkyl or aryl group), the compounds are called aldehydes. Aldehydes are named systematically by the substitution of the suffix '-al' for the suffix '-e' of the hydrocarbon, and ketones by the substitution of the suffix '-one'. Some of the common examples of the aldehydes and ketones are shown in Fig. 5.15.

$$
\begin{array}{ccc}
\overset{\displaystyle O}{\overset{\displaystyle \|}{H-C-H}} &
\overset{\displaystyle O}{\overset{\displaystyle \|}{CH_3-CH_2-CH_2-C-H}} &
\overset{\displaystyle H}{\overset{\displaystyle |}{CH_3-C=O}} \\
\text{Methanal} & \text{1-Butanal} & \text{Ethanal} \\
\text{(Formaldehyde)} & \text{(n-Butyraldehyde)} & \text{(Acetaldehyde)}
\end{array}
$$

$$
\begin{array}{ccc}
\overset{\displaystyle H}{\overset{\displaystyle |}{C_6H_5-C=O}} &
\overset{\displaystyle O}{\overset{\displaystyle \|}{CH_3-C-CH_3}} &
\overset{\displaystyle O}{\overset{\displaystyle \|}{CH_3-C-CH_2-CH_3}} \\
\text{Benzaldehyde} & \text{Dimethyl ketone} & \text{Methyl ethyl ketone} \\
\text{(Phenylmethanal)} & \text{(Acetone)} & \text{(Butanone)}
\end{array}
$$

$$
\overset{\displaystyle O}{\overset{\displaystyle \|}{CH_3-C-C_6H_5}}
$$
Acetophenone
(Methyl phenyl ketone)
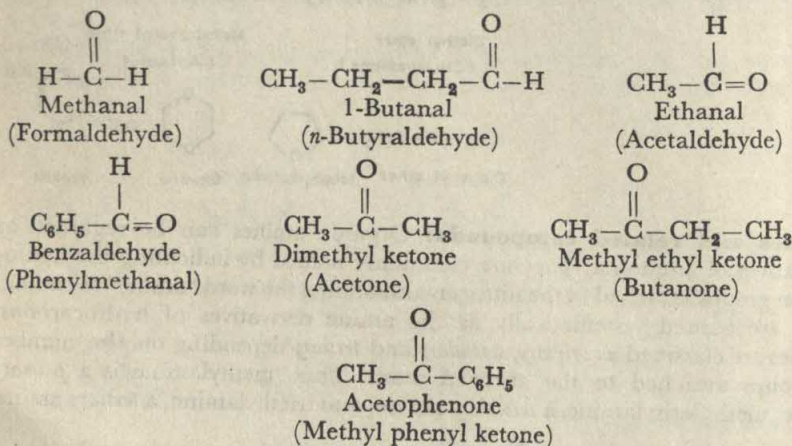
Fig. 5.15 Examples of aldehydes and ketones

In the carbonyl group, both the carbon and oxygen atoms are trigonally hybridised (sp^2) and are linked together by a σ bond. In addition, there is a π bond connecting carbon and oxygen due to the overlap of the unhybridised p orbitals of these two atoms. The two lone pairs of electrons around the oxygen occupy the remaining sp^2 orbitals (Fig. 5.16).
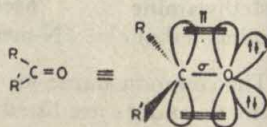
Fig. 5.16 Carbonyl group

Several naturally occurring products contain aldehydes and ketones. The naturally occurring *civetone*, obtained from the civet cat, is an example of a cyclic compound containing the unsaturated carbonyl group.
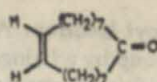
Civetone

Carboxylic acids: Carboxylic acids (RCO_2H) are derivatives of hydrocarbons containing the carboxyl (—CO_2H) group. The systematic naming is by adding the suffix ' -oic ' for the ending ' -e ' to the name of the longest straight chain in the molecule that includes the carbon of the carboxyl group and adding the word ' acid ' (methanoic acid, ethanoic acid, etc.). The systematic and common names of a few carboxylic acids are listed in Table 5.7.

Table 5.7 Some Carboxylic Acids

Systematic name	Common name	Structure	Systematic name	Common name	Structure
			Phenylmethanoic acid	Benzoic acid	
Methanoic acid	Formic acid	H-C-OH			
Ethanoic acid	Acetic acid	CH₃-C-OH	(2-Hydroxyphenyl)-methanoic acid	Salicyclic acid	
Propanoic acid	Propionic acid	CH₃-CH₂-C-OH			
Butanoic acid	Butyric acid	CH₃-CH₂-CH₂-C-OH			

A large number of carboxylic acids which occur in nature contain more than one carboxylic acid group. Some of these di- and tri-carboxylic acids are listed below:

$$
\begin{array}{c}
CO_2H \\
| \\
CO_2H
\end{array}
$$

Oxalic acid

$$
\begin{array}{c}
CO_2H \\
\diagup \\
CH_2 \\
\diagdown \\
CO_2H
\end{array}
$$

Malonic acid

$$
\begin{array}{c}
CH_2-CO_2H \\
| \\
CH_2-CO_2H
\end{array}
$$

Succinic acid

$$
\begin{array}{c}
CO_2H \\
\diagup \\
(CH_2)_3 \\
\diagdown \\
CO_2H
\end{array}
$$

Glutaric acid

$$
\begin{array}{cc}
H & CO_2H \\
\diagdown & \diagup \\
& C \\
& \| \\
& C \\
\diagup & \diagdown \\
HO_2C & H
\end{array}
$$

Fumaric acid

$$
\begin{array}{cc}
H & CO_2H \\
\diagdown & \diagup \\
& C \\
& \| \\
& C \\
\diagup & \diagdown \\
H & CO_2H
\end{array}
$$

Maleic acid

$$
\begin{array}{c}
H \\
| \\
HO-C-CO_2H \\
| \\
CH_2-CO_2H
\end{array}
$$

Malic acid

$$
\begin{array}{c}
H \\
| \\
HO-C-CO_2H \\
| \\
HO-C-CO_2H \\
| \\
H
\end{array}
$$

Tartaric acid

$$
\begin{array}{c}
CH_2-CO_2H \\
| \\
HO-C-CO_2H \\
| \\
CH_2-CO_2H
\end{array}
$$

Citric acid

Phthalic acid

Acyl halides: Acyl halides are derived from acids by replacing the hydroxyl group by a halogen. In naming acyl halides, the ending 'oic' of the carboxylic acid is changed to 'oyl' and the name of the halide is added. The names of some acyl halides are listed in Table 5.8.

Table 5.8 Some Acyl Halides

Systematic name	Common name	Structure	Systematic name	Common name	Structure
Ethanoyl chloride	Acetyl chloride	$CH_3-\overset{\overset{O}{\|\|}}{C}-Cl$	3-Methylbu-tanoyl chloride	Isovaleryl chloride	$CH_3-\overset{\overset{CH_3}{\|}}{CH}-CH_2-\overset{\overset{O}{\|\|}}{C}-Cl$
Propanoyl bromide	Propionyl bromide	$CH_3-CH_2-\overset{\overset{O}{\|\|}}{C}-Br$	Phenylme-thanoyl chloride	Benzoyl chloride	$C_6H_5-\overset{\overset{O}{\|\|}}{C}-Cl$

Anhydrides: Anhydrides contain two acyl groups bound to an oxygen atom. Anhydrides are named by adding the word 'anhydride' to the name of the acid.

$$CH_3-\overset{\overset{O}{\|\|}}{C}-O-\overset{\overset{O}{\|\|}}{C}-CH_3$$
Ethanoic anhydride
(Acetic anhydride)

$$C_6H_5-\overset{\overset{O}{\|\|}}{C}-O-\overset{\overset{O}{\|\|}}{C}-C_6H_5$$
Benzoic anhydride
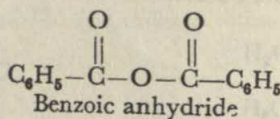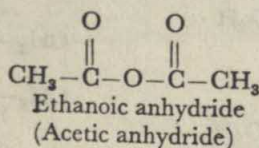
Esters and lactones: An ester is derived from the reaction of an alcohol and acid, with the elimination of water. Esters are pleasant smelling substances and are used in perfumes. Esters of carboxylic acids are named by specifying the group attached (from alcohol) and adding the suffix 'ate' in place of 'ic' in the name of the carboxylic acid (Fig. 5.17).

$H-\overset{\overset{O}{\|\|}}{C}-O-CH_3$
Methyl methanoate
(Methyl formate)

$CH_3-\overset{\overset{O}{\|\|}}{C}-O-CH_2-CH_3$
Ethyl ethanoate
(Ethyl acetate)

$C_6H_5-\overset{\overset{O}{\|\|}}{C}-O-CH_2-CH_3$
Ethyl benzoate

Methyl salicylate
(Oil of wintergreen)
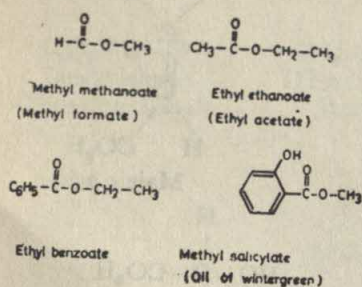
Fig. 5.17 Some common esters

Cyclic esters are referred to as *lactones* and are designated as β-, γ-, or δ-lactones depending on the ring size; β-lactones are exceedingly unstable substances. Examples of lactones are β-propiolactone, γ-butyrolactone, δ-valerolactone, etc.

β-Propiolactone   γ-Butyrolactone   δ-Valerolactone
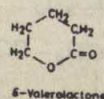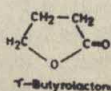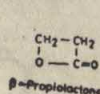
Amides: Replacement of the —OH group of an acid by an —NH₂ group gives amides. They can be described as acyl derivatives of ammonia or amines (Fig. 5.18). The names of amides are derived from the names of the correspond-
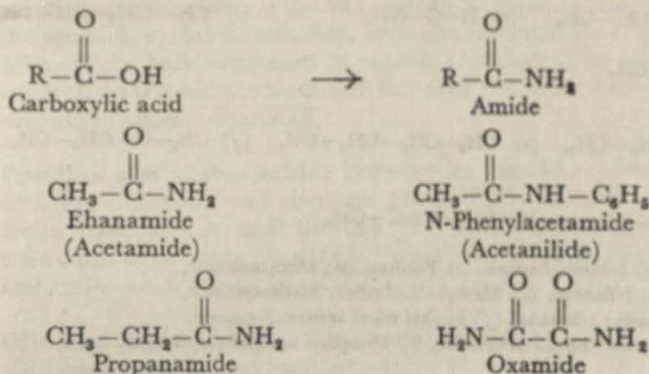
Fig. 5.18 Some amides

ing carboxylic acids by the substitution of the suffix ' amide ' for the ' ic ' acid endings. Amides are less basic than the amines due to the delocalisation of the lone pair of electrons on nitrogen by resonance. Thus, the C—N bond of an amide has considerable double bond character and free rotation about this is somewhat restricted.
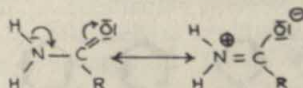
Example 5.4 Classify the following compounds under various categories based on their functional groups. In case of alcohols and amines, mention whether, *primary*, *secondary* or *tertiary*.

(a) CH₃—Cl

(b) CH₃—CH—OH
         |
        CH₂
        CH₃

(c) CH₃—C(=O)—OH

(d) CH₃—C(=O)—CH₃

(e) CH₃—C(CH₃)(—OH)—CH₃

(f) CH₃—CH₂—C(=O)—O—CH₃

(g) CH₃—O—CH₂—CH₃

(h) (CH₃—CH₂)₃N

(i) CH₃—C(=O)—Cl

(j) CH₃—CH₂—CH₂—OH

(k) CH₃—CH₂—NH₂

(l) CH₃—C(=O)—NH₂

(a) Alkyl chloride   (b) *sec*-Alcohol   (c) Carboxylic acid
(d) Ketone   (e) *tert*-Alcohol   (f) Ester
(g) Ether   (h) *tert*-Amine   (i) Acid chloride
(j) *primary* Alcohol   (k) *primary* Amine   (l) Acid amide

Example 5.5 Give both the common and the systematic names of the following:

(a) $CH_3—CH_2—\underset{\underset{CH_3}{|}}{CH}—CH_3$ (b) $H—\overset{\overset{O}{\|}}{C}—NH_2$ (c) $CH_3—CH_2—CH=CH_2$

(d) $CH_3—O—CH_2—CH_3$, (e) $CH_3—CH_2—CH_2—\overset{\overset{O}{\|}}{C}H$, (f) $CH_3—\overset{\overset{O}{\|}}{C}—CH_2—CH_3$,

(g) $CH_3—\overset{\overset{O}{\|}}{C}—Cl$,   (h) $CH_3—C\equiv C—CH_3$
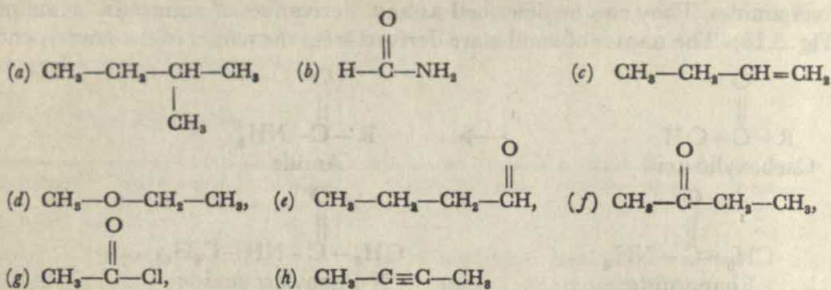
(a) *Iso*-pentane; 2-Methylbutane, (b) Formamide; Methanoamide,
(c) 1-Butylene; 1-Butene, (d) Methyl ethyl ether; Methoxyethane,
(e) Butyraldehyde; 1-Butanal, (f) Methyl ethyl ketone; Butanone,
(g) Acetyl chloride; Ethanoyl chloride, (h) Dimethyl acetylene; 2-Butyne.

5.1.3 Heterocyclic Compounds

Organic cyclic compounds containing hetero atoms such as oxygen, sulphur, nitrogen, etc., as part of the ring systems are referred to as heterocyclic compounds. Some examples of the common heterocyclic compounds are shown in Fig. 5.19. Many heterocyclic compounds occur in nature both in plants and animals. Industrially, some of these compounds are obtained from coal tar fractions.
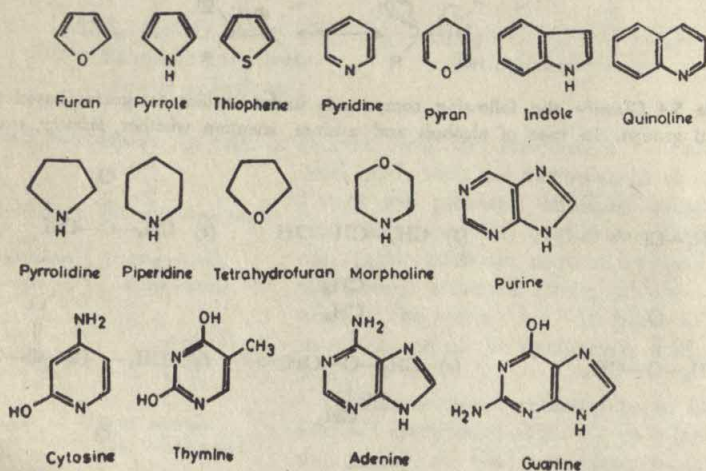
Fig. 5.19 Heterocyclic compounds

5.1.4 Compounds from Nature (Natural Products)

In earlier sections we have discussed in detail the different types of organic compounds and also the nature of the functional groups present in them. We shall now examine briefly some of the organic compounds which are produced in nature, and which are of everyday use.

Natural products are organic compounds which are derived from either plant or animal kingdom. A variety of natural products have been isolated from these sources and some of the important classes of natural products are proteins, carbohydrates, oils, fats, alkaloids, terpenes, and steroids. Of these, the proteins, carbohydrates, fats, and oils form important constituents of food. Many of the basic discoveries in organic chemistry have been made through research on natural products and this area continues to be challenging and exciting to organic chemists.

Proteins and amino acids: Proteins are important chemical constituents of living organisms and they are essentially large poly-
meric molecules formed through the combination of different amino acids. A detailed discussion of proteins and amino acids will be found in Chapter 18.

$$H_2C-O-\overset{\overset{\text{O}}{\|}}{C}-R$$
$$HC-O-\overset{\overset{\text{O}}{\|}}{C}-R$$
$$H_2C-O-\overset{\overset{\text{O}}{\|}}{C}-R$$
Oil or Fat

Oils and fats (Lipids): Oils and fats (butter, corn oil, cotton seed oil, groundnut oil, olive oil, etc.) are naturally occurring esters (glycerides) of the trihydroxy alcohol, glycerol, and high molecular weight carboxylic acids (fatty acids). They come under the general class of organic compounds which are referred to as *lipids*.

Most oils and fats contain different fatty acids rather than a single fatty acid. Some of the common fatty acids found in oils and fats are shown in Table 5.9. In general, oils are liquids and contain mainly unsaturated fatty acids, whereas fats are solids and contain predominantly saturated fatty acids. The catalytic hydrogenation of vegetable oils such as groundnut oil and cotton seed oil produces cooking butter or *vanaspati* (like *Dalda*). On hydrolysis with sodium hydroxide (saponification), both oils and fats are converted to the sodium salts of fatty acids (soap) and glycerol. Both these reactions are of industrial importance.

$$
\begin{array}{l}
H_2C-O-\overset{\overset{\text{O}}{\|}}{C}-R \\
HC-O-\overset{\overset{\text{O}}{\|}}{C}-R \quad + \;\; 3\,NaOH \;\longrightarrow \\
H_2C-O-\overset{\overset{\text{O}}{\|}}{C}-R
\end{array}
\qquad
\begin{array}{l}
H_2C-OH \\
HC-OH \quad + 3R-\overset{\overset{\text{O}}{\|}}{C}-O^{\ominus}Na^{\oplus} \\
H_2C-OH \qquad\qquad \text{Soap}
\end{array}
$$

Oil or Fat   Glycerol
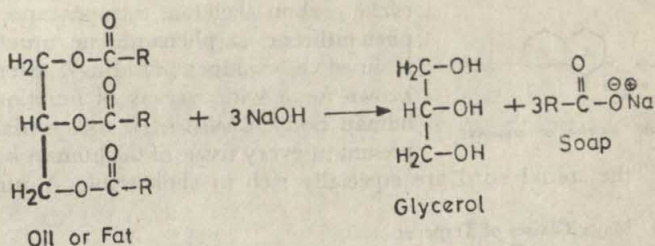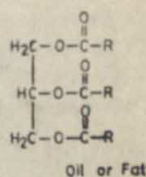
Table 5.9 Some Fatty Acids

Name of the acid	Structure
Lauric acid	$CH_3-(CH_2)_{10}-CO_2H$
Myristic acid	$CH_3-(CH_2)_{12}-CO_2H$
Palmitic acid	$CH_3-(CH_2)_{14}-CO_2H$
Stearic acid	$CH_3-(CH_2)_{16}-CO_2H$
Oleic acid	$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-CO_2H$
Linoleic acid	$CH_3-(CH_2)_4-CH=CH-CH_2-CH=CH-(CH_2)_7-CO_2H$

Alkaloids: Alkaloids (alkali-like substances) are basic, complex nitrogenous compounds of vegetable origin. They are related to heterocyclic compounds such as pyrrole, pyridine, quinoline, isoquinoline, and indole. Many alkaloids are highly toxic and possess remarkable physiological action. The use of *quinine* for malaria, *morphine* for relieving pain, *cocaine* as a local anaesthetic, *ephedrine* in the treatment of allergies, *reserpine* as a tranquiliser, and *strychnine* in heart diseases are well known examples of medicinal applications of alkaloids. The structures of quinine and reserpine are shown as illustrative examples below.

Quinine   Reserpine
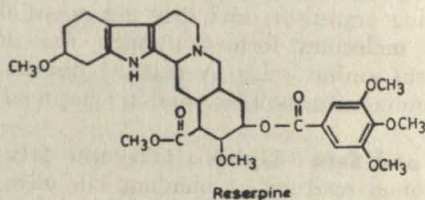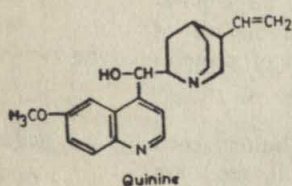
Terpenes: Terpenes are hydrocarbons or their oxygenated derivatives that are found mainly in the essential oils of plants. Many of these oils have been used as flavours and perfumes since centuries. The characteristic mono-meric structural unit present in all terpenes is isoprene (2-methyl-1, 3-but-adiene, C_5H_8); the terpenes are, there-fore, classified on the basis of the num-ber of isoprene units they contain.
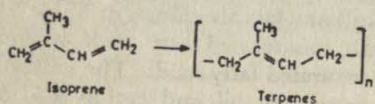
Isoprene   Terpenes

Some of the representative members of the various classes are shown in Table 5.10.

Steroids: Steroids are a group of natural products containing the tetra-cyclic carbon skeleton, cyclopentanoperhydro-phenanthrene (a phenanthrene unit to which is fused a cyclopentane ring). Steroids are known for a wide variety of functions in the human body. *Cholesterol* is a steroidal alcohol present in every tissue of the human being. The brain and the spinal cord are especially rich in cholesterol. A number of

Basic skeleton of steroids
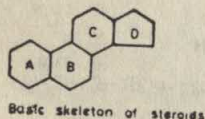
Table 5.10 Major Classes of Terpenes

Class	No. of isoprene units	Name of a represen- tative member and its source	Class	No. of isoprene units	Name of a representa- tive member and its source
Monoterpene	2	a-Pinene (Oil of turpentine)	Triterpene	6	Squalene (Liver of sharks)
Sesquiterpene	3	Zingiberene (Oil of ginger)	Tetraterpene	8	a-Carotene (Carrots)
Diterpene	4	Abietic acid (Pine rosin)	Polyterpene	n	Natural rubber

steroid acids, known as bile acids, occur in combined form in human and animal bile. They serve the function of aiding the digestion of fats and oils. The sex hormones, which control the sex characteristics and related biological functions in living organisms, are essentially steroidal derivatives.

Cholesterol
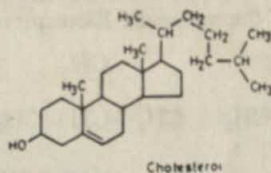
Carbohydrates: Carbohydrates are essentially polyhydroxy aldehydes (aldoses) or polyhydroxy ketones (ketoses) and they are commonly referred to as saccharides or sugars. The sugar that we employ in daily use is *sucrose* or cane sugar ($C_{12}H_{22}O_{11}$) and it is formed through the combination of two simpler sugars, *glucose* ($C_6H_{12}O_6$) and *fructose* ($C_6H_{12}O_6$).

As an illustrative example, we discuss the structure of glucose (Fig. 5.20). In a simplified, but not very accurate, representation of glucose (Structure A), all the six carbon atoms are shown to be linked through σ bonds in a linear fashion. However, we know that the properties of glucose can be better explained in terms of the cyclic structure B. Structure C is merely a different representation of the cyclic structure B.
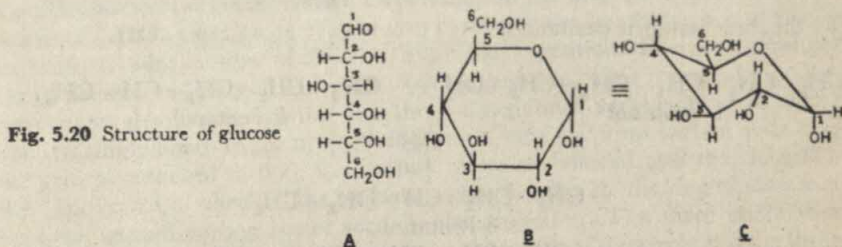
Fig. 5.20 Structure of glucose

Starch and cellulose are examples of carbohydrates which occur widely in plants. They are long chain ploymeric molecules containing glucose units and they can be chemically degraded to glucose under appropriate conditions (see Chapter 18).

5.2 ISOMERISM

Substances which differ in their chemical and physical properties, but have the same molecular formula are called *isomers*. For example, ethyl alcohol and dimethyl ether have the same molecular formula, C_2H_6O, and yet are distinctly different compounds. Isomerism is characteristic of complex molecules held together by covalent bonds and the difference between the various isomers is due to the differences in the arrangement of atoms in the molecule. Isomerism can be broadly classified under two types: *structural isomerism* and *stereoisomerism*.

5.2.1 Structural Isomerism
Structural isomers have different structural formulae in which the arrangement of atoms is different. Structural isomerism may be of different types, e.g. (*i*)

chain isomerism, (*ii*) position isomerism, (*iii*) functional group isomerism, and (*iv*) tautomerism.

Chain isomerism: Chain isomers differ in the arrangement of the atoms forming the 'backbone' of the molecule. Examples are the three pentanes.

$$CH_3—CH_2—CH_2—CH_2—CH_3 \qquad CH_3—\overset{\overset{\displaystyle CH_3}{|}}{CH}—CH_2—CH_3 \qquad CH_3—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—CH_3$$

$$\textit{n-Pentane} \qquad\qquad\qquad Isopentane \qquad\qquad\qquad Neopentane$$
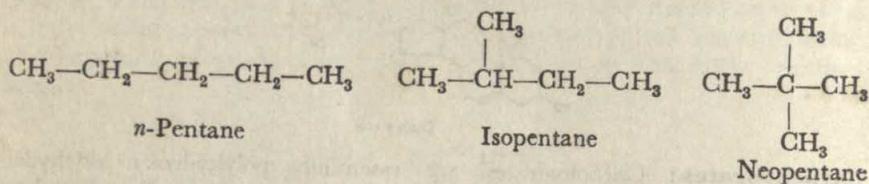
Position isomerism: Position isomers have the same carbon skeleton but differ in the postition of the attached atom or group. Examples are:

(*a*) the three dibromobenzenes,

o - Dibromobenzene   m - Dibromobenzene   p - Dibromobenzene
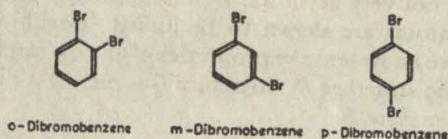
(*b*) the three isomeric pentanols,

$$CH_3—CH_2—CH_2—CH_2—CH_2—OH \qquad CH_3—CH_2—CH_2—\overset{\overset{\displaystyle OH}{|}}{CH}—CH_3$$
$$\text{1-Pentanol} \qquad\qquad\qquad\qquad\qquad \text{2-Pentanol}$$

$$CH_3—CH_2—\overset{\overset{\displaystyle OH}{|}}{CH}—CH_2—CH_3$$
$$\text{3-Pentanol}$$
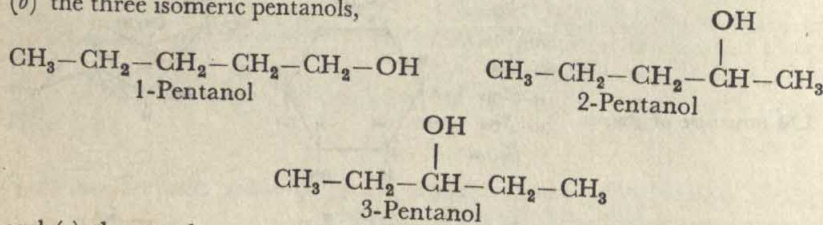
and (*c*) the two butenes, $CH_3—CH_2—CH=CH_2$ $\qquad$ $CH_3—CH=CH—CH_3$
$$\text{1-Butene} \qquad\qquad\qquad \text{2-Butene}$$

Functional group isomerism: The same atoms can be rearranged to form molecules that differ from one another in the functional groups they carry. For example, the molecular formula C_2H_6O may represent ethyl alcohol ($CH_3—CH_2—OH$) as well as dimethyl ether ($CH_3—O—CH_3$). This is an example of functional group isomerism.

Tautomerism: Many functional group isomers are easily interconvertible, and exist in dynamic equilibrium. Such isomers are referred to as tautomers. Tautomers are isolable under appropriate conditions. A good example of tautomerism is the case of carbonyl compounds. Nitromethane and aci-nitromethane are also tautomers.

Keto form of acetone   Enol form of acetone   Nitromethane   Aci-nitromethane

Organic Molecules
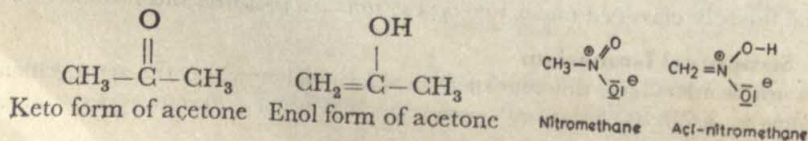
Example 5.6 Write the structural formulae for all the chain isomers of compounds represented by molecular formula C_6H_{14}.

(a) $CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$

(b) $CH_3—CH_2—CH—CH_2—CH_3$
$\qquad\qquad\qquad\qquad\quad |$
$\qquad\qquad\qquad\qquad\quad CH_3$

(c) $CH_3—CH—CH_2—CH_2—CH_3$
$\qquad\quad\;\; |$
$\qquad\quad\;\; CH_3$
$\qquad\quad\;\; CH_3$
$\qquad\quad\;\; |$

(d) $CH_3—CH—CH—CH_3$
$\qquad\qquad\quad |$
$\qquad\qquad\quad CH_3$

(e) $CH_3—C—CH_2—CH_3$
$\qquad\quad\;\; |$
$\qquad\quad\;\; CH_3$
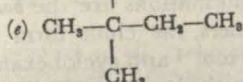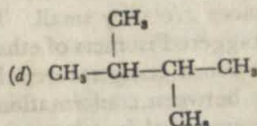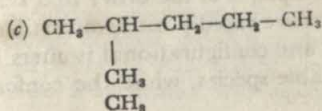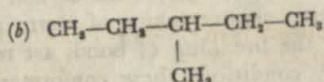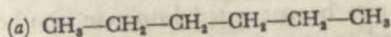
5.2.2 Stereoisomerism

Isomers that differ *only* in the spatial arrangement of the constituent atoms are called stereoisomers and the arrangement of atoms that characterises a particular stereoisomer is called its *configuration*. The different types of stereoisomerism are: (*i*) conformational isomerism, (*ii*) geometrical isomerism, and (*iii*) optical isomerism.

Conformatiomal isomerism: Depending on the angular relationship between the hydrogens attached to the two carbon atoms in ethane, the molecule can have a large number of differing atomic arrangements. Two such arrangements are shown in Fig. 5.21 by the *Newman projection*. This representation is a convenient device for showing the three-dimensional arrangement of atoms about a single bond. In the projection formula, only the front carbon atom and the groups attached to both the carbon atoms are viewed and they look like the 'spokes of a wheel'. The carbon–carbon bond is in the line of view and thus the second carbon is not seen in the projection. The three bonds that are attached to the front carbon stem from the centre of the circle and the three other bonds project from the edge or margin of the circle. In Fig. 5.21, ethane molecule is shown in the *staggered* arrangement in which the hydrogen atoms on the adjacent carbons are staggered and are as far apart as possible. In the other arrangement, three pairs of hydrogen atoms *eclipse* each other. Eclipsing leads to steric repulsion of *hydrogen* atoms that are not directly bonded. In the case of ethane, this non-bonded interaction (between the eclipsed hydro-

Staggered conformation   Eclipsed conformation
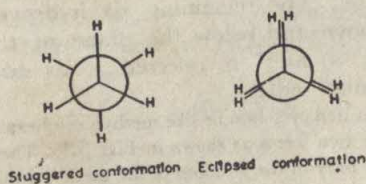
Fig. 5.21 Newman representation of the staggered and eclipsed conformations of ethane

Fig. 5.22 (Right) Potential energy changes during rotation about carbon–carbon bond of ethane
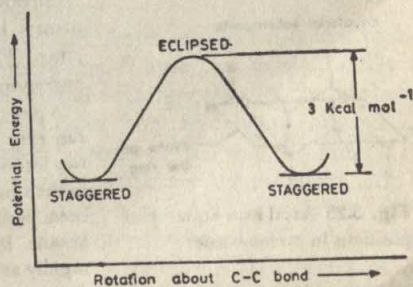
gen atoms) raises the energy of the eclipsed arrangement by about 3 kcal mol^{-1}. The change from one arrangement to another in such stereoisomers involves a rotation about the carbon–carbon bond (Fig. 5.22).

Different arrangements of atoms that can be converted into one another without the breaking of bonds are referred to as *conformers* or *rotamers*. Under ordinary conditions these conformers are not isolable intermediates as their energy differences are very small. The energy difference between the fully eclipsed and staggered isomers of ethane, for example, is of the order of 3 kcal mol^{-1}, and at room temperature, these isomers are rapidly interconvertible. The difference between conformational isomers and configurational isomers is that the configurational isomers are stable, isolable species, while the conformational isomers are not.

In the case of cyclohexane (C_6H_{12}) the extreme conformations are the *boat* and *chair* forms shown in Fig. 5.23. Of these two isomers, the chair form is more stable than the boat conformation by about 6 kcal mol^{-1} and cyclohexane exists mostly in the chair form at room temperature. In the boat form, several

Boat conformation   Chair conformation
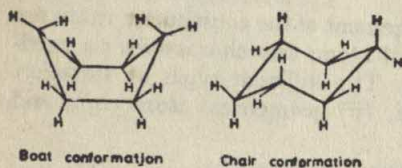
Fig. 5.23 Boat and chair conformations of cyclohexane
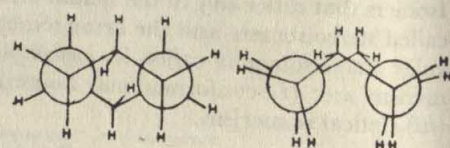
Fig. 5.24 Newman projection formulae of the boat and chair conformations of cyclohexane

of the hydrogen atoms are in the eclipsed arrangement and therefore, steric repulsions among these atoms will be appreciable in this isomer. As against this,

Axial substituents

Equatorial substituents

Plane of the ring

Fig. 5.25 Axial and equatorial positions in cyclohexane

all the hydrogen atoms in the chair conformation are fully staggered and are as far apart as possible. The Newman projection formulae (Fig. 5. 24) clearly indicate the arrangement of the hydrogen atoms in both boat and chair forms of cyclohexane.

The twelve hydrogen atoms (or substituents) in the chair form of cyclohexane are of two distinct types—six of these lying in a plane around the cycle of carbon atoms and these are figuratively designated as *equatorial hydrogens* (symbolised *e*). The remaining six hydrogen atoms lie above and below the plane of the ring (Fig. 5.25) and are referred to as *axial hydrogens* (symbolised *a*).

A monosubstituted cyclohexane like methylcyclohexane can exist in the two forms as shown in Fig. 5.26. These two forms differ only in the positions of the methyl group in the ring (axial or equatorial). In practice, it has not been possible to isolate the two forms of methylcyclohexane. It appears that the two forms interconvert very rapidly at room temperature causing a substituent in the axial position to go to an equatorial position and vice versa. Ordinary methylcyclohexane is an
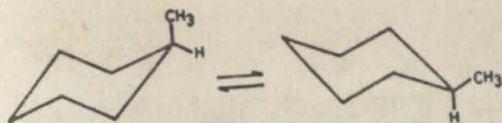
Fig. 5.26 Methylcyclohexane
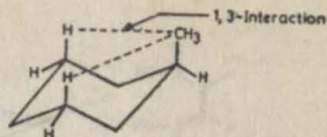
Fig. 5.27 Steric repulsions in the axial isomer of methylcyclohexane

equilibrium mixture of both the axial and equatorial substituted isomers. However, there is enough evidence to show that non-bonded steric repulsions due to the two axial hydrogens and the methyl group (Fig. 5.27) are greater in the axial isomer which explains why the axial isomer is less stable than the equatorial one.

Example 5.7 Starting with the most stable conformation, write the Newman projection formulae of all conformers of 1-chloropropane (CH_3–CH_2–CH_2–Cl), obtained by rotation about C_1–C_2 bond through angles of 60°, 120°, 180°, 240°, 300° respectively. Indicate the staggered and eclipsed conformations.

| Staggered (most stable) | Eclipsed (60°) | Staggered (120°) | Eclipsed (180°) | Staggered (240°) | Eclipsed (300°) |
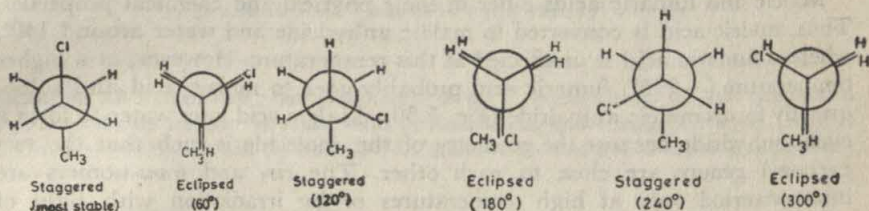
Geometrical isomerism: Geometrical isomerism is another type of stereoisomerism arising out of different spatial arrangements of groups attached to double bonds (carbon–carbon double bonds or double bonds between carbon and other atoms) or rings in which the stereoisomers are not readily interconvertible. We have already seen that a carbon–carbon double bond consists of a σ bond and a π bond, formed by the overlap of the *p* orbitals that lie above and below the plane of the sp^2 orbitals. The overlap of the *p* orbitals restricts the rotation about carbon–carbon double bond (Fig. 5.28) and geometrical isomers arise as a result of this *restricted rotation.*

Overlap of p orbitals No overlap of p orbitals
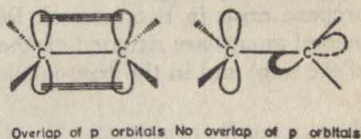
Fig. 5.28 Rotation of carbon–carbon double bond prevents the overlap of *p* orbitals

Butenedioic acid, HO_2C—CH=CH—CO_2H, for example exists in two isomeric forms. These two isomers differ in the spatial arrangement of the carboxyl groups and the hydrogens around the carbon atoms. In one isomer, the carboxyl groups are on the same side of the double bond and is referred to as the *cis*-isomer, whereas in the other the *trans*-isomer, the carboxyl groups are *trans* with respect to each other (on

Maleic acid (cis) Fumaric acid (trans)
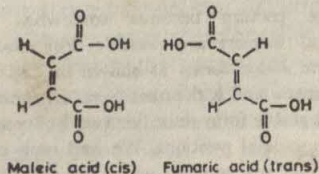
Fig. 5.29 *cis*- and *trans*-Isomers of butenedioic acid
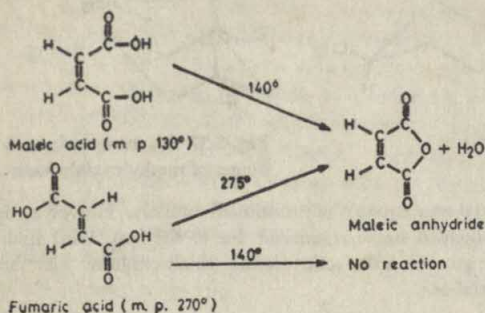
Fig. 5.30 Conversion of fumaric acid to maleic acid

opposite sides). Geometrical isomerism is also referred to as *cis–trans* isomerism. The two forms of butenedioic acid are commonly known as maleic acid and fumaric acid respectively (Fig. 5.29).

Maleic and fumaric acids differ in their physical and chemical properties, Thus, maleic acid is converted to maleic anhydride and water around 140°, whereas fumaric acid is unaffected at this temperature. However, at a higher temperature ($\sim$275°) fumaric acid probably goes to maleic acid and subsequently forms maleic anhydride (Fig. 5.30). Maleic acid loses water to form a cyclic anhydride because the geometry of the molecule is such that the two carboxyl groups are close to each other. The *cis*- and *trans*-isomers are interconverted only at high temperatures or by irradiation with light of suitable wavelength. The interconversion of isomers involves the breaking of the π bond of the carbon–carbon double bond followed by rotation about the carbon–carbon σ bond and subsequent reformation of a new π bond.

Cyclic compounds also exhibit *cis–trans* isomerism. Thus, 1, 2-dimethylcyclopropane exists in two isomeric forms (Fig. 5.31). In the *cis*-isomer, both the methyl groups are situated on the same side (either above or below the plane of the ring) and in the *trans*-isomer, the methyl groups are on opposite sides.

cis-1,2-Dimethylcyclopropane   trans-1,2-Dimethylcyclopropane
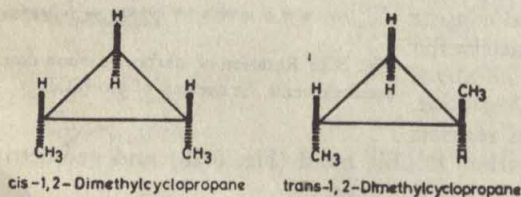
Fig. 5.31 *cis*- and *trans*-Isomers of 1, 2-dimethylcyclopropane

In the case of substituted cyclohexanes, the picture becomes somewhat more complicated — both geometrical and conformational isomers are possible. For example, 4-*t*-butylcyclohexyl chloride can exist in four isomeric chair forms as shown in Fig. 5.32. Structures *c* and *d* represent the *cis*-isomers and structures *a* and *b*, the *trans*-ones. Of these four isomers, the one represented by structure *a* is the most stable form since the two bulky substituents (*t*-butyl and chlorine) in this isomer are in equatorial positions. We had seen earlier that non-bonded steric repulsions in a cyclohexane ring are minimal when the substituents occupy equatorial positions. Between structures *c* and *d*, structure *c* represents a more stable isomer, as the more bulky of the two substituents in this isomer, namely, the *t*-butyl group is in equatorial position.
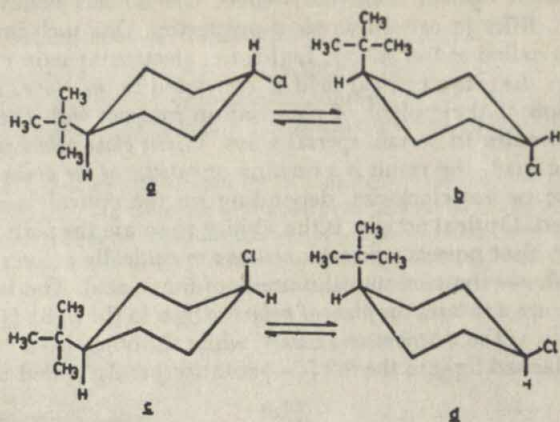
Fig. 5.32 Isomeric forms of 4-*t*-butylcyclohexyl chloride

Example 5.8 Remembering that substituents in the *e* positions cause the least non-bonded repulsion, decide whether the substituents in the following cyclohexane derivatives, (*a*) *cis*-1, 2-Dimethylcyclohexane and (*b*) *trans*-1, 2-Dimethylcyclohexane are in *aa*, *ae* or *ee* positions,
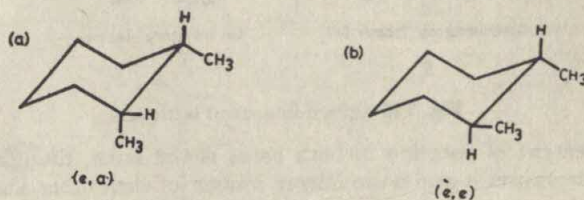
Optical isomerism: The spatial disposition of atoms in a given molecule may impart a certain amount of symmetry to the molecule in much the same way that the packing of ions or molecules in a crystal does (Chaper 7). Consider a molecule like formaldehyde, CH_2O. Rotation of the molecule around the $C = O$ bond does not produce any new configurational arrangement that is different from the original; i.e. the molecule possesses a certain rotational symmetry. Similarly, we may reflect the molecule about the vertical plane, and it remains unchanged, since it also has a reflection symmetry. It is possible to classify molecules into various symmetry groups, depending on their behaviour to symmetry operations like the ones mentioned. On the other hand, there exist molecules in nature wherein the atoms are arranged in a fashion that imparts no sense of symmetry to the molecule. Consider a lactic acid molecule, which has four different groups attached to the central carbon atom. If we perform a reflection operation, i.e. look at the mirror image of lactic acid, the image is no longer superimposable on the original molecule. The mirror image is, in fact, realised to be an isomer, differing in absolute spatial configuration from the original. These two lactic acid molecules, which are not superimposable on their mirror images, form a pair of what are called *optical isomers*. Many naturally occurring

compounds exhibit optical isomerism, where the isomers behave identically chemically, but differ in certain physical properties. One such important property is what is called *optical activity*. Light, i.e. electromagnetic radiation, can be *polarised* such that its electrical field is restricted to *one plane*. Photons with such a restriction of their plane of polarisation interact with the electrons in atoms and molecules in certain special ways. When *plane polarised light* is irradiated on lactic acid, the result is a turning or *rotation of the plane of polarisation* either clockwise or anticlockwise, depending on the optical isomer of lactic acid that is used. Optical activity is the ability to rotate the plane of polarised light. Molecules that possess *asymmetric centres* are optically active.

Figure 5.33 shows the two optical isomers of lactic acid. The isomers represented by structure *a* rotates the *plane of polarised light* to the right [(+) rotation] and is referred to as the *dextrorotatory isomer*, while the other (structure *b*) rotates the plane of polarised light to the left [(−) rotation] and is called the *levorotatory*
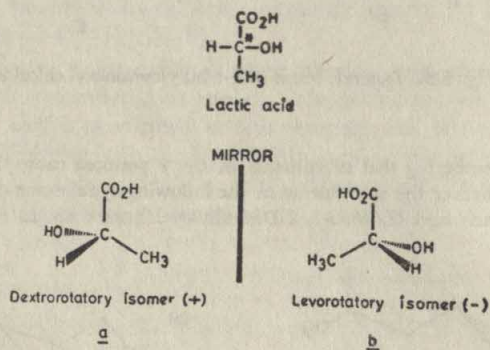
Fig. 5.33 Optical isomers of lactic acid

isomer. The extent of rotation in both cases is the same, though in opposite directions. Structures *a* and *b* are mirror images of each other and are known as *enantiomers*.

When equal amounts of both isomers are mixed, the rotation caused by the molecules of the dextro-isomer (+) is counterbalanced by the rotation of the levo-isomer (−) and the mixture as a whole shows no rotation, i.e. it is optically inactive. Such a mixture of equal amounts of the dextro- and levo-isomers is called a *racemic mixture*. From a racemic mixture, both (+) and (−) isomers can be isolated by suitable methods and this process of separation is known as *resolution*. Conversion of an optically active isomer into a racemic mixture is called *racemisation*.

The angle by which polarised light is rotated by an optically active substance can be measured using a polarimeter. The extent of rotation caused by any optically active compound is characteristic of that asymmetric substance, its concentration (in solution), the wavelength of the plane polarised light used, the temperature, and the solvent. The angle of rotation is commonly expressed in terms of the *specific rotation*, which is defined by the following expression,

$$\left[a \right]_{\lambda}^{t^{\circ}} = \frac{a}{lC}$$

where a is the observed rotation in degrees; λ, the wavelength of light source; t° the temperature; C the concentration in grams of sample per millilitre; and

l the length of the solution in decimetres. For example, when the specific rotation of a compound is indicated as $[\alpha]_D^{25°} = +37\cdot5°$ ($C = 0\cdot15$, chloroform), it means that this substance has a specific rotation of $+37\cdot5°$ at a concentration of $0\cdot15$ g per ml of chloroform solution at $25°$, when contained in a tube 1 decimetre long, the rotation being measured using sodium light (wavelength, 5893 A).

When the number of asymmetric centres in a molecule increases, the number of possible isomers also increases. Thus, there are four possible isomers for 2, 3-dihydroxybutanoic acid, a substance which contains two asymmetric carbons. All these isomers are known and they can be represented by structures (a, b, c, and d) as shown in Fig. 5.34. Of these four forms, a is the mirror image of b and these two isomers have equal rotations of opposite sign. These two are
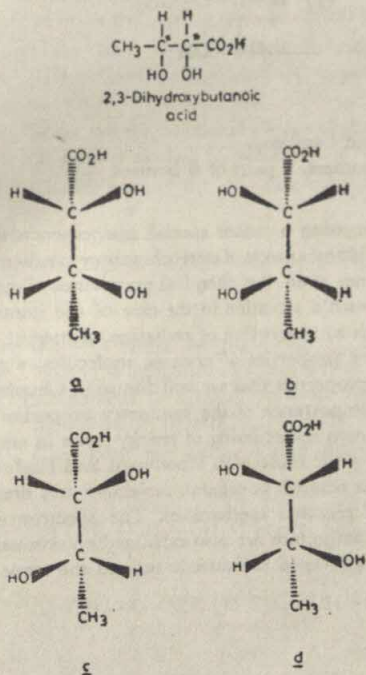
Fig. 5.34 Isomers of 2, 3-dihydroxybutanoic acid
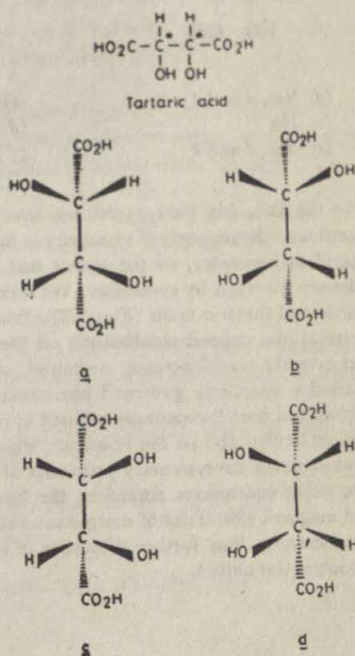
Fig. 5.35 Isomers of tartaric acid

enantiomers. Similarly, c and d form another enantiomeric pair of isomers. However, the relationship between a and c or between b and d is quite different. These isomeric pairs differ in their chemical and physical properties and are not enantiomers. Stereoisomers which are not enantiomers (and thereafter are not mirror images) are called *diastereoisomers* (or diastereomers).

Tartaric acid is another example of an organic compound containing two asymmetric carbon atoms. Unlike 2, 3-dihydroxybutanoic acid, tartaric acid exists only in three isomeric forms. The different forms of tartaric acid can be represented by structures a, b, c and d as shown in Fig. 5.35. Of these, structures a and b represent two optically active forms whose chemical and physical properties are identical, but the only difference being in their optical properties. These two form a pair of enantiomers. Structures c and d appear to be different on paper, but they are identical and are superimposable (rotation of c in the plane of the paper through $180°$ will give d). Structure c or d represents one isomer of tartaric acid which has a plane of symmetry bisecting the bond between the two asymmetric carbon atoms. This isomer

of tartaric acid is optically inactive and is referred to as *meso*-tartaric acid. *meso*-Tartaric acid and either one of the optically active forms of tartaric acid *a* or *b* are diastereomers.

Example 5.9 Which of the following compounds would exhibit optical activity? State how many isomers are possible for those that do?

$$
(a)\quad CH_3-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CO_2H
\qquad
(b)\quad \underset{\underset{Cl}{}\diagdown\ \diagup\underset{Br}{}}{\overset{H\diagdown\ \ \diagup H}{C=C}}
\qquad
(c)\quad CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3
$$

$$
(d)\quad CH_3-\underset{\underset{HO}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3
\qquad
(e)\quad Cl-\underset{\underset{I}{|}}{\overset{\overset{F}{|}}{C}}-Br
\qquad
(f)\quad Br-\underset{\underset{HO}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3
$$
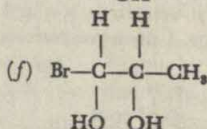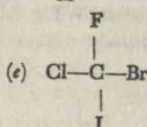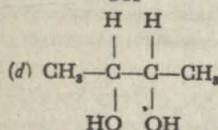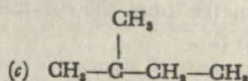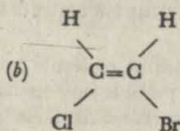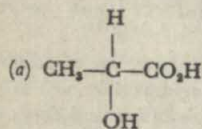
(a) Yes, *d* and *l*   (b) No

(c) No   (d) Yes, *d* and *l* and *meso*

(e) Yes, *d* and *l*   (f) Yes, 4 isomers, 2 pairs of *dl* isomers

In the foregoing paragraphs, we have been discussing a rather special phenomenon that accentuates the property of symmetry in molecules. Many aspects of stereochemistry are directly related to symmetry, to the extent that many times even the chemical reactivities of molecules are governed by symmetry. We encountered such a situation in the case of the isomers, maleic and fumaric acids (Fig. 5.30). Processes such as absorption of radiation, scattering, or emission also depend significantly on the symmetry properties of crystals, molecules, atoms and even the wavefunctions. Anisotropy of several properties that we will discuss in Chapter 7 is another symmetry governed phenomenon. The importance of the symmetry properties of orbitals has been increasingly realised in recent years in the ordering of energy levels in atoms and molecules, and in the reaction pathways of organic molecules. Woodward and Hoffman have analysed the symmetry properties of molecular orbitals in organic molecules and drawn interesting conclusions regarding the feasibility of reaction mechanisms. The spectroscopic and magnetic properties of inorganic coordination compounds are also explained on symmetry considerations. Any further discussion of symmetry governed processes is beyond the scope of a book of this nature.

SUGGESTED READING

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PROBLEMS

5.1 Explain briefly the type of hybridisation in methane, ethylene and acetylene.

5.2 What shapes would you expect the following molecules or ions to have?
(a) CH_3^+, (b) CH_3^-, (c) NH_4^+, (d) NH_2^- and (e) CH_3—O—CH_3

5.3 Draw the atomic orbital models for each of the following substances. Be sure that the orbitals occupied by unshared pairs as well as those used in bond formation are correctly labelled.

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{}}$$

(a) CH_3—Cl, (b) CH_3—C—H, (c) CH_3—CH_2—OH, (d) CO_2,
(e) $(CH_3)_2NH$, and (f) CH_3—C≡C—CH_3

5.4 Indicate the structural similarities and differences resulting from trigonal (sp^2) hybridisation of the valence electrons of carbon in ethylene and of boron in borontrichloride.

5.5 What are the states of hybridisation of each carbon atom in butatriene ($CH_2=C=C=CH_2$) and 1, 3-butadiene ($CH_2=CH$—$CH=CH_2$)? Sketch $\sigma-\pi$ models of these molecules.

5.6 What are the functional groups of the following class of organic compounds: (a) Ether, (b) *primary* alcohol, (c) aldehyde, (d) carboxylic acid, (e) *secondary* amine, and (f) ester?

5.7 Classify each of the following compounds according to its functional group:

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{}}$$

(a) CH_3—O—CH_2—CH_3, (b) $(CH_3)_2NH$, (c) CH_3—CH_2—C—CH_2—CH_3

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{}} \qquad \overset{\displaystyle OH}{\overset{\displaystyle |}{}}$$

(d) CH_3—CH_2—C—OH, and (e) CH_3—CH—CH_2—CH_3

5.8 Write the structures and names of all possible alkyl, alkenyl and aryl groups which after attachment of a hydrogen atom may give the following compounds: (a) Isobutane, (b) *n*-Butane, (c) ethylene, and (d) benzene.

5.9 Give both the common and the systematic names of the following: (a) CH_2Cl_2,

$$\overset{\displaystyle OH}{\overset{\displaystyle |}{}} \qquad\qquad \overset{\displaystyle O}{\overset{\displaystyle \|}{}}$$

(b) CH_3—CH_2—$CH=CH_2$, (c) CH_3—CH_2—CH—CH_3, (d) CH_3—CH_2—C—Cl,

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{}} \qquad\qquad \overset{\displaystyle NH_2}{\overset{\displaystyle |}{}}$$

(e) CH_3—C—NH_2 (f) CH_3—CH—CH_3, (g) CH_3—CH_2—O—CH_3, and

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{}}$$

(h) CH_3—C—CH_3.

5.10 Write the structures for the following compounds: (a) Butyric acid, (b) *p*-aminophenol; (c) *sec*-butyl bromide, (d) methyl vinyl ether, (e) allyl alcohol, (f) 2-butyne, (g) methyl formate, and (h) N, N-dimethylformamide.

5.11 Give an example of each of the following and name them: (a) Neutral α-amino acid, (b) basic α-amino acid, and (c) acidic α-amino acid.

5.12 Write the structural isomers of the compound represented by molecular formula C_5H_{10}.

5.13 Consider the substance $BrCH_2$—CH_2Br. Draw a graph of potential energy versus angle of rotation for the conformers of this molecule. Let 0° represent the eclipsed conformation and show a continuous plot from 0° to 360°. Use Newman projection formulae to show the relative position of atoms in space corresponding to 0°, 60° and 180°.

5.14 State which of the following pairs of compounds you would expect to be more stable, and why? (a) *cis-* or *trans-*1, 3-dibromocyclohexane, (b) *cis-* or *trans-*1, 2-dimethylcyclopropane and (c) *cis-* or *trans-*1-methyl-4-*tert*-butylcyclohexane.

5.15 Which of the following molecules can show *cis-trans* isomerism? Draw the structures of the isomers and label them *cis* or *trans*. (*a*) 2-methyl-2-pentene, (*b*) 2-methyl-3-hexene, (*c*) 1, 3-dimethylhexane, (*d*) 1, 2-dichlorocyclobutane, and (*e*) propenylbenzene.

5.16 Of the structures listed below (*i*) which may display geometrical isomerism and (*ii*) which may display optical isomerism?

$$\text{(a) } CH_3-CH=CH-CH_3, \quad \text{(b) } \underset{\displaystyle \overset{|}{Cl}}{\overset{\displaystyle \overset{Cl}{|}}{CH_3-CH_2-C-CH_3}}, \quad \text{(c) } \underset{\displaystyle \overset{|}{Br}}{\overset{\displaystyle \overset{Br}{|}}{CH_3-C-CO_2H}},$$

$$\text{(d) } \underset{\displaystyle \overset{|}{}}{\overset{\displaystyle \overset{Cl}{|}}{CH_3-CH=CH-CH-CH_3}}, \text{ and (e) } Cl_2C=C(CH_3)_2$$
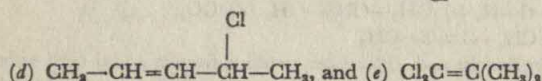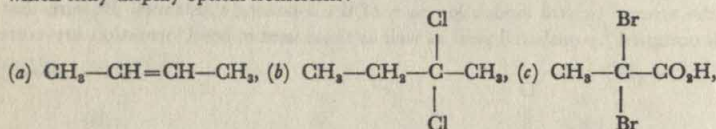
5.17 From the list of formulae below, select those which best fit each description: (*a*) a *cis*-stereoisomer, (*b*) a pair of diastereoisomers, (*c*) a *meso* compound, (*d*) a pair of enantiomers, and (*e*) a pair of compounds which might form a racemic mixture.

$$(CH_3)_2C=C(CH_3)-CH_2-CH_3, \quad \underset{Cl}{\overset{Br}{\diagdown}}C=C\underset{Cl}{\overset{H}{\diagup}}, \quad \underset{H}{\overset{CH_3}{\diagdown}}C=C\underset{CH_3}{\overset{H}{\diagup}},$$

$$\begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ CH_3 \end{array}, \quad \begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ CHO \end{array}, \quad \begin{array}{c} CHO \\ | \\ HO-C-H \\ | \\ HO-C-H \\ | \\ CH_3 \end{array}, \quad \begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ HO-C-H \\ | \\ CH_3 \end{array}$$
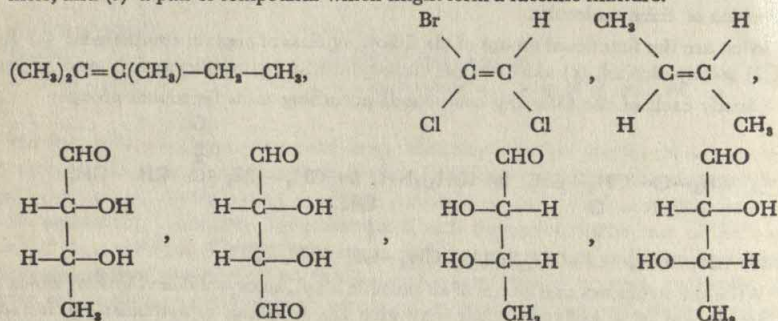
5.18 Describe the relationship between each pair of structures given below:

$$\text{(a) } \overset{\displaystyle \overset{O}{\|}}{CH_3-CH_2-C-CH_2-CH_3}, \quad \overset{\displaystyle \overset{O}{\|}}{CH_3-C-CH_2-CH_2-CH_3}$$

$$\text{(b)} \quad \underset{H}{\overset{CH_3}{\diagdown}}C=C\underset{H}{\overset{CH_3}{\diagup}}, \quad \underset{H_2C}{\overset{H}{\diagdown}}C=C\underset{H}{\overset{CH_3}{\diagup}}$$

$$\text{(c) } \overset{\displaystyle \overset{O}{\|}}{CH_3-C-CH_2-CH_3}, \ \overset{\displaystyle \overset{OH}{|}}{CH_2-C=CH-CH_3}$$

$$\text{(d) } CH_2=CH-O-CH_2-CH_2-CH_2-CH_3,$$

$$\text{(e) } \overset{\displaystyle \overset{CO_2H}{|}}{H_2N-C-H} \ , \quad \overset{\displaystyle \overset{CO_2H}{|}}{H-C-NH_2}$$
$$\qquad \underset{CH_3}{} \qquad\qquad \underset{CH_3}{}$$
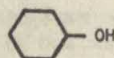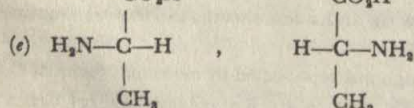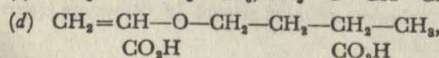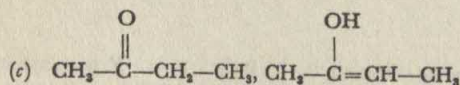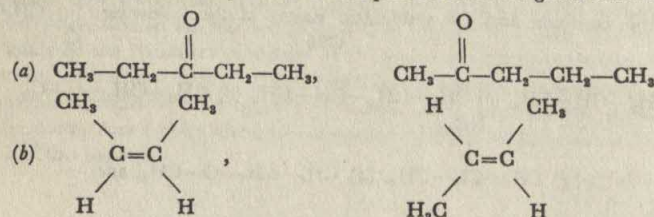
5.19 Benzene hexachloride ($C_6H_6Cl_6$) gives rise to six isomeric compounds. Write the structure of each of the isomers and indicate which chlorine atoms are axial or equatorial.

5.20 Make sketches of the following, specifying whether the substituents are axial or equatorial. Also indicate whether they can be optically active: (*a*) *cis*-1, 2-dichlorocyclohexane, (*b*) *cis*-1, 3-dichlorocyclohexane, and (*c*) *cis*-1, 4-dichlorocyclohexane.
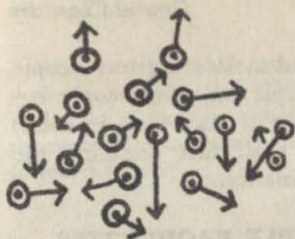
6

The Gaseous State

Imagine the air to be such a heap of little bodies, lying one upon another, as may be resembled to fleece of wool.

ROBERT BOYLE

A vacuum is nothing and what is nothing cannot exist.

THOMAS HOBBES

As the pressure increased, the volume of the gas decreased.

ROBERT BOYLE

I have no data yet. It is a capital mistake to theorise before one has data. Insensibily one begins to twist facts to suit theories instead of theories to suit facts.

'SHERLOCK HOLMES'

Gases, liquids and solids constitute the three principal states of matter. For example ice, water and steam are the three states of the same substance, water. Depending upon the temperature and pressure, a substance exists in one of these three states. Nitrogen, the main constituent of air, is a solid below its melting point ($-210°C$); below its normal boiling point ($-196°C$), it is a liquid. As will be shown later, under certain conditions of temperature and pressure, characteristic of each pure substance, the three states of matter can be in equilibrium and exist indefinitely in contact with one another.* For example, at $-210°C$, a closed container filled with nitrogen contains gaseous, liquid and solid nitrogen (Fig. 6.1). Solid nitrogen remains at the bottom of the container since it is densest and is covered by the less dense liquid nitrogen; above the liquid nitrogen is the gaseous nitrogen at a pressure of 100 mm Hg.

According to atomic–molecular theory discussed earlier we know that matter is made up of molecules which in turn are made of atoms. Individual atoms and molecules have certain intrinsic (microscopic) properties, but in this chapter, we shall be concerned only with the behaviour of bulk matter.† One of the main objectives of modern chemistry is to relate the properties of a large collection of molecules which constitute the matter in bulk (macroscopic

*Such conditions exist at the triple point which will be discussed in Chapter 10.
†By bulk (or macroscopic), we mean a sample of matter (gas, liquid or solid) weighing more than, say, 10^{-3} g and therefore, containing something like 10^{19} molecules or more.

properties) to the properties of individual atoms and molecules (microscopic properties). Since such a relation between macroscopic and microscopic behaviour is simpler in gases than in solids or liquids, we shall first examine the gaseous state of matter.

6.1 MEASURABLE PROPERTIES OF GASES

Before discussing the behaviour of gases, we shall examine certain properties of gases which can be measured experimentally. The important properties are: (1) Mass (or number of molecules), (2) volume, (3) pressure, and (4) temperature.

Mass: The mass of a gas can be determined by weighing a container in which the gas is enclosed and weighing the container again after removing all the gas. The difference between the two weights gives the mass of the gas. The mass is related to number of moles by the equation,

$$\text{MOLES} = \frac{\text{MASS IN GRAMS}}{\text{MOLECULAR MASS}}$$

We recollect here that 1 mole of a substance contains 6.02×10^{23} molecules.

Fig. 6.1 Gas, liquid and crystal (solid) phases of nitrogen in equilibrium at the triple point

Volume: The volume of a substance is the space occupied by the substance. Since gases tend to occupy the whole space available to them, the measurement of the volume of a gas only requires a measurement of the volume of the container confining the gas. As the volume of unit mass of water is accurately known, the volume of the container is readily obtained by weighing the water required to fill the container.

Generally, the volume is specified in units of litres, millilitres (ml) or cubic centimetres (cc). As the name implies 1 cc is the volume of a cube of 1 cm length, 1 cm breadth and 1 cm height. A litre on the other hand was not formerly considered as derived from units of length, but it was defined as the volume occupied by one kilogram of water at 4°C when the density of water is maximum. Thus,

1 litre = 1000·028 cc or 1 ml = 1·000028 cc

However, 1 ml is now defined to be exactly equal to 1 cc.

Pressure: Pressure is force per unit area. Gases exert pressure (or force) on the interior walls of the vessels in which they are confined, or in other words, gases exert pressure on all boundaries with which they are in contact.

A convenient method for measuring atmospheric pressure utilises a device known as a mercury *barometer*. A barometer can be made by filling a long tube (longer than 76 cm) closed at one end with mercury and inverting the tube in an open vessel of mercury (Fig. 6.2). The mercury level in the tube drops until the mercury column exerts a downward pressure on the mercury

in the open vessel which is exactly balanced by the atmospheric pressure. Under these conditions, the mercury in the tube falls to a height approximately 76 cm (or 760 mm) above the level of the mercury in the open vessel. When the atmospheric pressure increases, the height of the mercury column rises; when the pressure of the atmosphere decreases, the height of the column decreases.

Fig. 6.2 Mercury barometer. Pressure of atmosphere = pressure of mercury column = h cm = 76 cm = 760 mm at standard atmospheric pressure and 0°C. (The empty space above the mercury was considered by Torricelli as a perfect vacuum, but today we know that it does contain a small number of mercury molecules.)
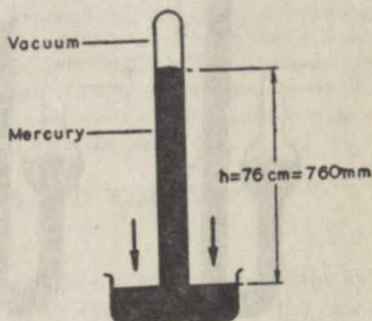
The pressure expressed in terms of the height of the mercury column can be converted into units of force per unit area. A mercury column h cm high and A cm^2 in cross-section exerts a downward force equal to the weight of the mercury and the force on unit area of surface is given by P.

$$P = \frac{\text{FORCE}}{\text{AREA}} = \frac{\text{MASS} \times \text{ACCELERATION}}{A} = \frac{m\,g}{A}.$$

where m is the mass of the mercury in the tube and g the acceleration due to gravity. If the density of mercury is ρ, then the mass of the mercury in the tube is given by ρV, where V is the volume of the mercury in the tube. The volume is given by Ah. Thus,

$$P = mg/A = \rho Vg/A = \rho Ahg/A = \rho hg$$

By international agreement, a standard pressure of one atmosphere (1 atm) is defined as the pressure exerted by exactly 76 cm (exactly 760 mm) of mercury at 0°C (density, 13·5951 g/cc) and at standard gravity, 980·665 cm s^{-2}. Therefore,

$$1 \text{ atm} = 13 \cdot 5951 \,\frac{\text{g}}{\text{cc}} \times 76 \cdot 0 \text{ cm} \times 980 \cdot 665 \,\frac{\text{cm}}{\text{s}^2}$$

$$= 1 \cdot 013 \times 10^6 \,\frac{\text{g} \cdot \text{cm}}{\text{cm}^2 \cdot \text{s}^2} = 1 \cdot 013 \times 10^6 \,\frac{\text{dynes}}{\text{cm}^2}$$

Further, 1 atm = 76·0 cm of mercury (cm Hg)
= 760 mm of mercury (mm Hg*) = 760 torr†

Gas pressures are usually measured by a device called the *manometer*. A manometer can be of either closed-end or open-end type (Fig. 6.3). In the closed-end manometer, the space above the mercury column is evacuated and hence the pressure of the gas can be read off directly in terms of mercury height. The open-end manometer has one arm open to the atmosphere and the quantity directly measured is known as gauge pressure; to this, the atmospheric pressure must be added to obtain the value of the gas pressure.

Temperature: We are familiar with the observation that when a hot body is placed in contact with a cold body, the former gets colder while the latter gets hotter till both of them eventually become equally hot. This is explained

*Hereafter pressure expressed in mm Hg will be denoted by mm.
†Unit named after Torricelli, inventor of the barometer.
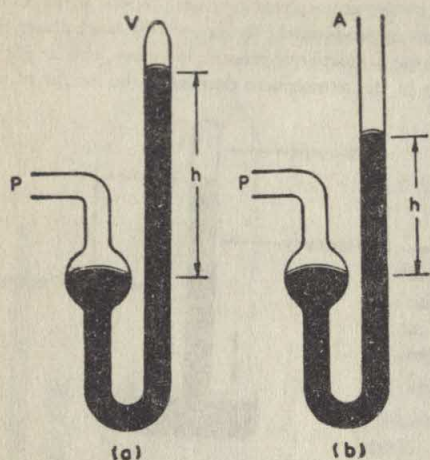
Fig. 6.3 Manometers (*a*) closed end and (*b*) open end (*P*, pressure source; *V*, vacuum; *A*, atmosphere). In (*a*) *h*, the difference in mercury levels, indicates the absolute pressure of the source. In (*b*), *h* indicates gauge pressure. To obtain absolute pressure, one must add the prevailing atmospheric pressure, i.e. *P* (source) = *h* + atmosphere pressure.

by saying that heat flows from the hot body to the cold body. The hot body is said to be at a higher temperature and the cold body at a lower temperature. Thus, temperature determines the direction of heat flow, but does not give the quantity of heat.
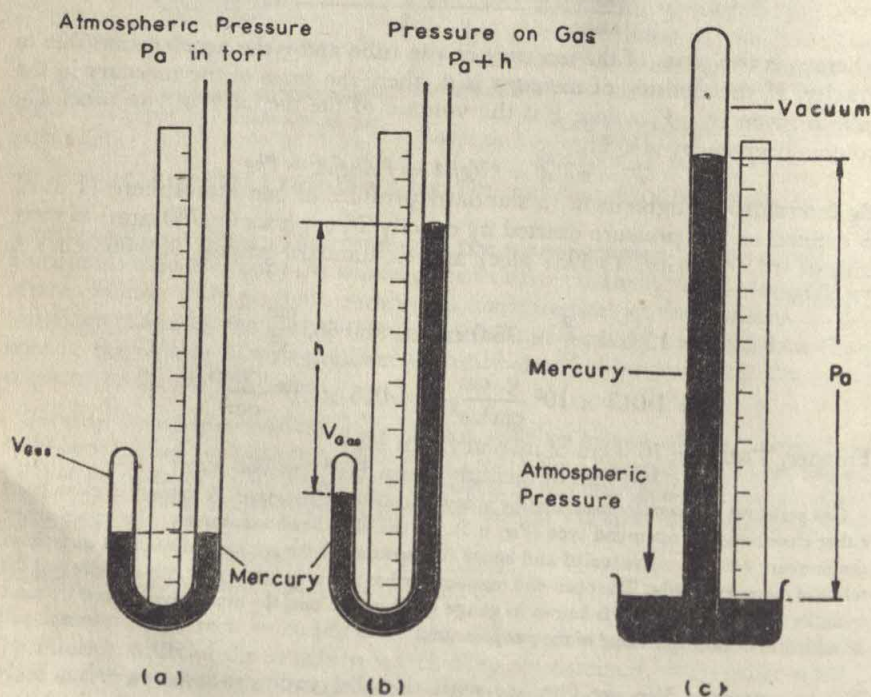
Fig. 6.4 The simple *J*-tube apparatus used by Boyle to measure pressure and volume. The pressure on the entrapped air is increased by adding mercury to the tube. In (*a*) the gas pressure is equal to the atmospheric pressure; in (*b*) the gas pressure is equal to $h + P_a$ where P_a is the atmospheric pressure; and (*c*) barometer.

The measurement of temperature is based on properties such as expansion of substances, which depend on the changes of temperature. Expansion of mercury is commonly made use of to measure temperature. For the *centigrade scale* (also known as *celsius* scale), the normal freezing point of water (0°C) and the boiling point of water at one atmospheric pressure (100°C) are taken as reference points and this range is divided into one hundred equal parts (so that each division corresponds to 1°C). Since the zero in the centigrade scale is arbitrarily fixed, it is possible to have negative temperature on the centigrade scale corresponding to the temperature below the freezing point of water. It may appear that the centigrade scale can be extended to infinitely negative temperatures, but experimental behaviour of gases (which will be discussed later) shows that temperatures below $-273\cdot15$°C are impossible to attain (see section 6.4).

6.2 RELATION BETWEEN PRESSURE AND VOLUME OF A GAS—BOYLE'S LAW

Amongst the earlier quantitative measurements on the gaseous state were those of Robert Boyle who studied in 1662 the effect of pressure* on the volume of a fixed mass of air, devising an apparatus which is very simple by modern standards. Using a bent tube and some liquid mercury (Fig. 6.4), Boyle found
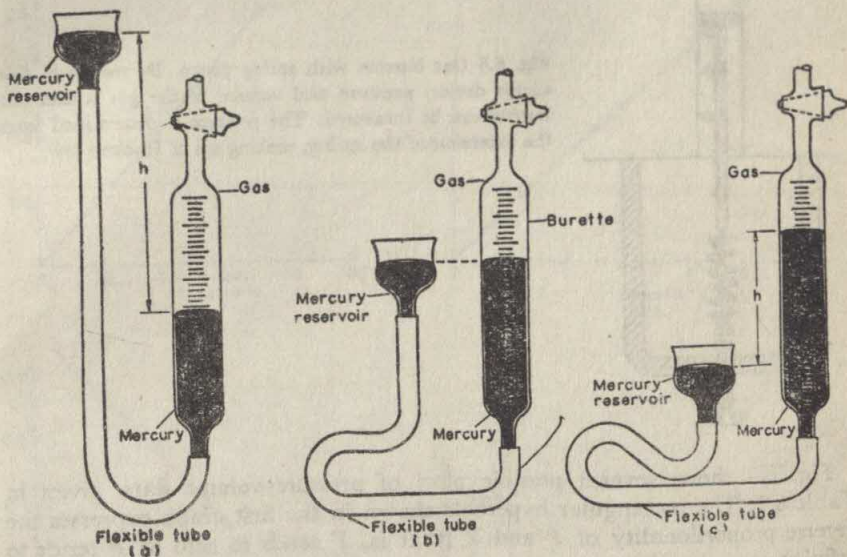
Fig. 6.5 Gas burette for demonstrating how a change in pressure effects the volume of a gas at constant temperature. The pressure on the gas is increased by raising the mercury reservoir and the volume of the gas is measured by the calibrated burette.

(a) Gas pressure=atmospheric pressure (P_a)+pressure due to mercury (h)
(b) Gas pressure=atmospheric pressure (P_a)
(c) Gas pressure+pressure due to mercury (h)=atmospheric pressure (P_a)
    or Gas pressure=atmospheric pressure (P_a)−pressure due to mercury (h).

that the length of the trapped air (to which the volume of the air was directly proportional) varied inversely with pressure applied to it. Boyle performed the

*Interestingly Boyle called pressure, *the spring of air*. Boyle's concept of air as an elastic fluid was closely associated with the idea of an atmosphere which exerted a definite pressure. On this basis, he tried to explain the pressure or the 'spring' of air.

experiment in a room where the temperature was approximately constant and he only needed a bent tube, liquid mercury, a barometer, and a measuring rule for his experiment. Boyle, of necessity, worked only with air, but when other gases were discovered it was soon found that they also showed inverse relationship between volume and pressure at constant temperature. The relationship between volume and pressure can be conveniently studied with the help of a gas burette (two kinds of gas burettes are shown in Figs. 6.5 and 6.6). Some of the results obtained with air using a gas burette (like the one shown in Fig. 6.5.) are given in Table 6.1.
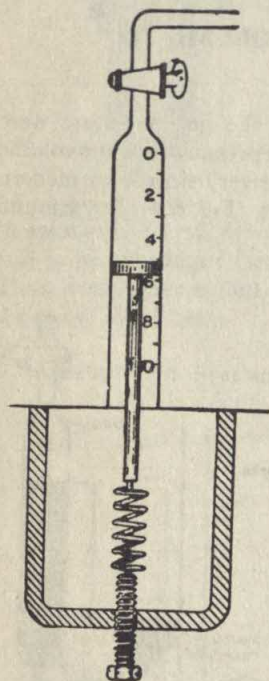
Fig. 6.6 Gas burette with spring piston. By means of this simple device, pressure and volume of the gas within the burette can be measured. The pressure is determined from the extension of the spring, making use of Hooke's law.

Fig. 6.7 shows several possible plots of pressure–volume data given in Table 6.1. The rectangular hyperbola shown in the first graph expresses the inverse proportionality of P and V (that is, V tends to zero as P tends to infinity or vice versa).

The plot of P versus V^{-1} (or $1/V$) is a straight line passing through the origin and so is the plot of V versus P^{-1} (or $1/P$). The plot of the logarithm of P versus the logarithm of V is also a straight line with a negative slope of one (i.e. slope $= -1$). The plot of the PV-product versus P is constant. These relations can be written as,

$$P = \text{CONST}/V \text{ or } V = \text{CONST}/P \text{ or } \log P = \text{CONST} - \log V \text{ or } PV = \text{CONST}$$

The above equations represent the different formulations of *Boyle's law* which can be stated as follows:

(*i*) For a given mass of gas,* the pressure is inversely proportional to the volume if the temperature is held constant, or

*The term ' given mass of gas ' or ' certain mass of gas ' is used to show that the amount of materials (or the number of moles of the material) does not change during the experiment. Thus

Table 6.1 Effect of pressure on the volume of a Gas (Air) at Constant Temperature

Pressure, P atm	Volume, V (litre)	PV (litre atm)
0·20	112·0	22·4
0·25	89·2	22·3
0·35	64·2	22·47
0·40	56·25	22·50
0·60	37·40	22·44
0·80	28·1	22·48
1·00	22·4	22·40
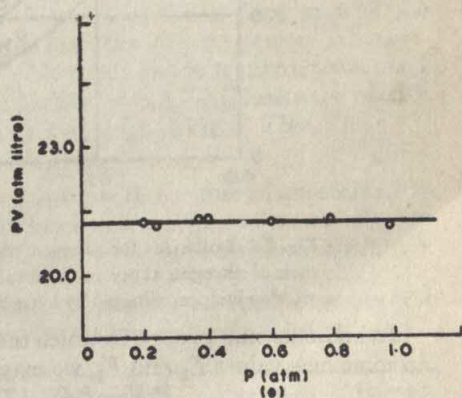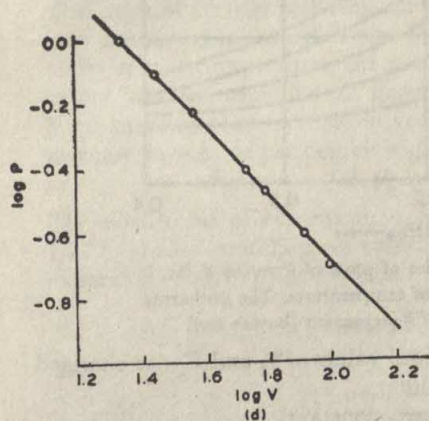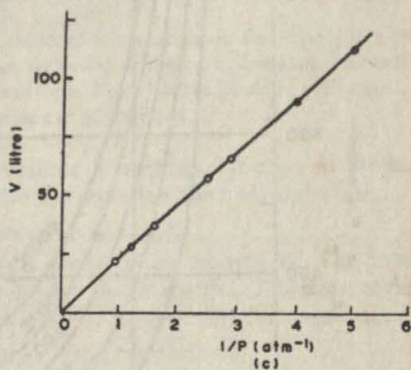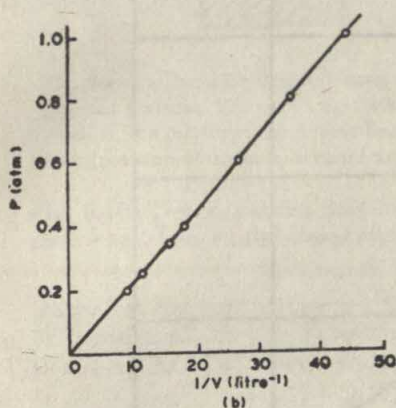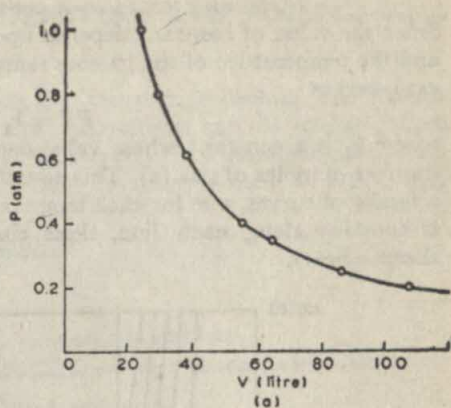
Fig. 6.7 Various ways of expressing Boyle's law

(*ii*) For a given mass of gas, the product of the volume and the pressure (*PV*) is a constant at constant temperature.

the term ' for a given mass of gas at constant temperature ', means that whereas pressure and volume *may change*, the temperature and the mass (or the number of moles being studied) *do not*.

PRESSURE × VOLUME = A CONSTANT   (n, T are constant)
Since the value of constant depends upon the mass (or the number of moles) and the temperature of the gaseous sample, Boyle's law can be more explicitly expressed as

$$PV = k_1 \ (n, T)$$

where k_1 is a constant whose value depends upon temperature (T) and the number of moles of gas (n). This equation for fixed n, can be represented by a family of curves, one for each temperature (Fig. 6.8). Since the temperature is constant along each line, these curves are called *isotherms* (iso=same, therm=heat).
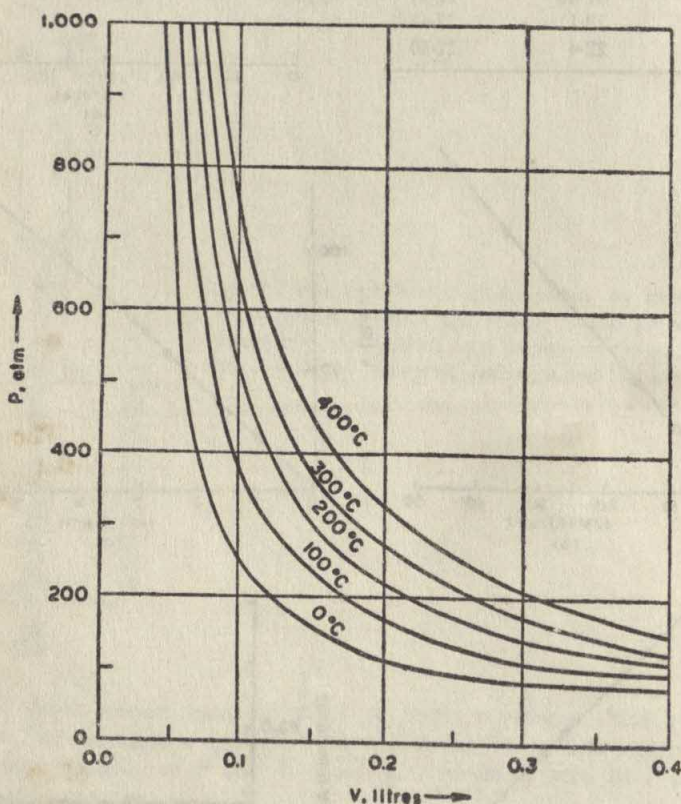
Fig. 6.8 Isotherms for nitrogen. A series of plots of P versus V for 1 mole of nitrogen at several fixed values of temperatures. The isotherms are closely approximated by hyperbola PV=constant (Boyle's law).

In an isothermal process in which the initial values of P_1 and V_1 are changed to some new values P_2 and V_2, we may write

$$P_1 V_1 = P_2 V_2 \quad (T, n \text{ are constant})$$

This relation is useful for the determination of the volume of a gas at any pressure, if its volume at any other pressure is known.

More accurate measurements reveal that gases do not exactly obey Boyle's law under all conditions; nevertheless Boyle's law provides a very useful approximation to the actual behaviour of most real gases.

6.3 RELATION BETWEEN TEMPERATURE AND VOLUME OF A GAS—CHARLES' LAW

We know that gases expand on heating and contract on cooling. The quantitative relationship between temperature and volume can be studied by an apparatus illustrated in Fig. 6.9. Table 6.2 records the volume measured on a sample of gas at several temperatures; these data are plotted on a graph in
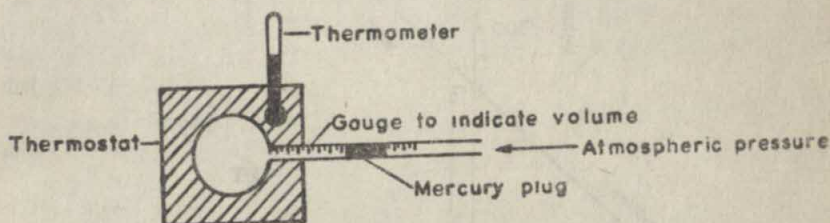
Fig. 6.9 Apparatus for demonstrating the effect of temperature on the volume of a gas at constant pressure. The gas in the flask can be heated or cooled at constant (atmospheric) pressure, the mercury plug moving back and forth. Note that the pressure of the gas in the flask (pressure=force/area) is equal to pressure of atmosphere.

Fig. 6.10. The plot shows that the volume is a linear function of the temperature and hence can be expressed by the equation for a straight line,

$$V = mt + C$$

where t is the temperature in °C and m and C are constants. The intercept on the vertical axis, C, is V_0 which is the volume at $t=0$°C. The slope of the line is $m=\Delta V/\Delta t$. The above equation can be written in the equivalent form

$$V=V_0+(\Delta V/\Delta t)t \qquad (n, p \text{ are constant})$$

The work of Charles and Gay-Lussac who made a series of volume–temperature measurements on different gases, showed that for a fixed mass of gas under a constant pressure, the relative increase per degree increase in temperature was the same for all gases on which they made measurements. At a fixed pressure, the increase in volume per degree is $\Delta V/\Delta t$, hence the relative increase in volume per degree is given by $a=(1/V_0)(\Delta V/\Delta t)$. Thus,

$$V=V_0+V_0at=V_0(1+at)$$

The coefficient of expansion, a, is a constant with a value of approximately 1/273. Under conditions of constant pressure and number of moles, all gases expand by 1/273 of their volume at 0°C for each degree rise in temperature.

Table 6.2 Changes in Volume of a Fixed Mass of Gas With Temperature (Pressure remains Constant)

Temperature °C	K	Volume ml	Temperature °C	K	Volume ml
−50	223	223	50	323	323
0	273	273	100	373	373
10	283	283	150	423	423
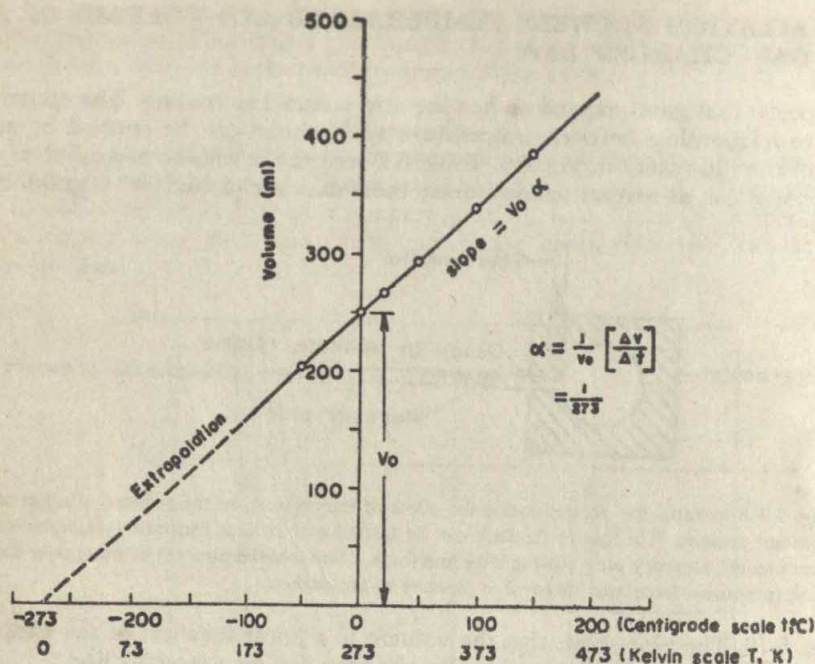
Fig. 6.10 A plot of volume versus temperature data (Table 6.2) showing that at constant pressure, V and t obey the linear equation $V = mt + C$. The constant m is the slope and can be determined from the graphical plot. Extrapolation of the line to zero volume indicates that $-273°C$ is the lowest temperature possible.

If a gas at 0°C is warmed to 1°C at constant pressure, the volume is increased by 1/273 of its original value; if the temperature is increased by 10°, the volume is increased by 10/273 of the value at 0°C; if the temperature is increased by 273 degrees, the increase in volume is 273/273 of its volume at 0°C, hence at 273°C the volume is double that at 0°C. On the other hand, if the gas is cooled by 1 degree, the volume of the gas decreases by 1/273 of its value at 0°C. If the gas is cooled to $-273°C$ (i.e. 273° below the melting point of ice) its volume would become zero. This result is of considerable interest and forms the basis of a new temperature scale discussed below.

6.4 ABSOLUTE SCALE OF TEMPERATURE

If we extrapolate the straight line in Fig. 6.10 beyond the actual measurements (the broken line in the figure), we find that it intersects the horizontal axis at $-273°C$. This shows that the volume of the gas would become zero at $-273°C$.* More precisely, this temperature is $-273\cdot15°C$ and is called the *absolute zero* of temperature since any temperature lower than this would cor-

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*A pertinent question is, 'Does this mean that if we cool a gas sufficiently at constant pressure, it disappears altogether?' The answer, of course, is no. What happens is that when cooled sufficiently, all gases liquefy and in the liquid form, they no longer obey either Boyle's or Charles' law. However this does not invalidate our graphic extrapolation to a hypothetical volume of zero. So the ideal gas in its strictest sense, is a hypothetical gas that does not liquefy but continues to obey Charles' law and shrinks until it finally occupies no volume.

respond to a negative volume of gas. This temperature has been approached experimentally, but has never been reached. Special methods have been used to approach within about 0·0001 of absolute zero.

In view of the fact that −273·15°C corresponds to a limiting value of zero volume, Lord Kelvin, who investigated the properties of gases extensively, proposed that a new scale of temperature be established in which the zero point corresponds to the value of temperature at which the volume of an ideal gas becomes equal to zero. He suggested the name *absolute temperature* and the symbol T to denote temperature value on this scale. It is now called the Kelvin scale of temperature and temperature on this scale is denoted by degrees Kelvin (K).

The absolute temperature scale, or the Kelvin temperature scale, is actually the centigrade scale with the zero moved down by 273·15 degrees.*

Absolute zero	−273·15°C	0 K
Ice point	0°C	273·15 K
Boiling point	100°C	373·15 K

Notice that the temperatures on the two scales are related by the equation, $T° = t° + 273$

The expression for the temperature-dependence of volume can now be expressed in terms of Kelvin (absolute) scale of temperature. Rearrangement of the equation gives

$$V = V_0(1 + t/273)$$
$$\text{(or)} \quad V/V_0 = (273 + t)/273$$

On the Kelvin scale, 273 is the temperature corresponding to V_0 ($t = 0°C$) and can be denoted as T_0 and we can write the above equation as,

$$(V/V_0) = (T/T_0)$$
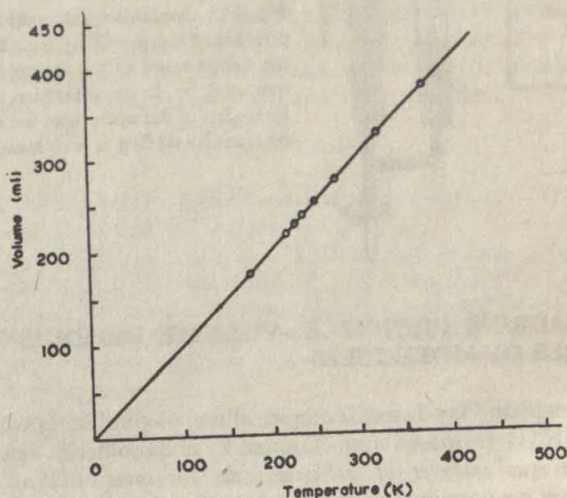
Fig. 6.11 A plot of data of Table 6.2 showing that volume is directly proportional to the absolute temperature

*Except where high accuracy is required, the value 273 is often used instead of 273.15.

This implies that volume of a gas varies directly with the absolute temperature. This result (Fig. 6.11) is known as *Charles' or Gay Lussac's law* which states that at constant pressure, the volume of a given mass of gas is directly proportional to its absolute temperature:

VOLUME = A CONSTANT × TEMPERATURE   (n, P are constant)

$V = k_2 T$ (n, P are constant), or

$V = k_2 (n, P) T$ (since k_2 depends on the mass and pressure of the gas)

Therefore,

$$(V_1/T_1) = (V_2/T_2)   (n, P \text{ are constant})$$

6.5 PRESSURE–TEMPERATURE RELATIONSHIP

If the temperature of a gas is altered keeping the volume constant, the pressure of the gas changes (Fig. 6.12). As in the case of volume, the pressure changes by 1/273 of its value at 0°C for each one degree change of temperature. The pressure increases with rise in temperature and decreases with fall in temperature. Thus,

PRESSURE = A CONSTANT × TEMPERATURE   (n, V are constant)

$P = k_3 T$ (n, V are constant) or $P = k_3 (n, V) T$

Therefore, $(P_1/T_1) = (P_2/T_2)$ (n, V are constant)
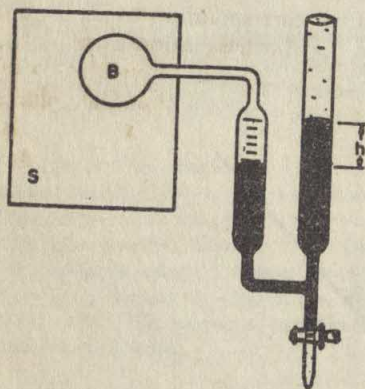
Fig. 6.12 Constant volume gas thermometer. The pressure of the gas filling bulb B is determined by the temperature of the system S. This pressure is indicated by h, the difference in mercury levels. By means of the open tube, the gas volume is kept constant by adding or withdrawing mercury.

6.6 AVOGADRO'S PRINCIPLE—VOLUME DEPENDENCE ON THE NUMBER OF MOLECULES

In order to explain Gay-Lussac's empirical law of combining volumes, Amedeo Avogadro (1811) proposed (see Chapter 2) a hypothesis: *Equal volumes of all gases contain equal number of molecules under the same conditions.* This implies that volume is proportional to the number of molecules.

It may be recalled that the amount of gas is measured in moles and that one mole of any gas contains the same number ($6 \cdot 02 \times 10^{23}$) of molecules. In terms of moles, *Avogadro's hypothesis* may be expressed as *equal volumes of gases contain the same number of moles* or volume is directly proportional to the number of moles. In equation form,

VOLUME = A CONSTANT × NUMBER OF MOLES

(Temperature and pressure held constant)

$V = k_4 n$ (T, P = constant)

or more explicitly, $V = k_4$ (T, P)n.

6.7 IDEAL GAS EQUATION OF STATE

In order to see how Boyle's law, Charles' law and Avogadro's principle can be combined, let us consider a quantity of gas occupying volume V_1 at temperature T_1 and pressure P_1 and ask the question what volume this gas will occupy at some different pressure P_2 and temperature T_2. This change can be carried out in two steps:

$$P_1 V_1 T_1 \xrightarrow{\text{STEP I}} P_2 V_x T_1 \xrightarrow{\text{STEP II}} P_2 V_2 T_2$$
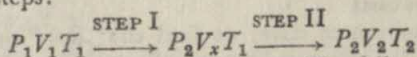
In step I, the temperature is kept constant at T_1 while pressure and volume change to P_2 and V_x; in step II, the pressure is kept constant at P_2 while volume and temperature change to V_2 and T_2.

In the first step T is constant and Boyle's law can be used to obtain $V_x = P_1 V_1 / P_2$. In the second step P is constant, and Charles' law can be used to obtain $V_x = V_2$ (T_1 / T_2). Combining these two equations, we get,

$$\frac{P_1 V_1}{P_2} = \frac{V_2 T_1}{T_2} \quad \text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

This result implies that the ratio of the product of P and V to the absolute temperature T is constant for a quantity of a particular gas. We may state it mathematically as, $(PV/T) = K(n)$, where K, the constant depends upon the kind and the quantity of the gas. To make this equation applicable to all gases, one must make use of Avogadro's principle. We know that the volume of a gas at constant temperature and pressure is directly proportional to the number of moles. This means that K is directly proportional to the number of moles of gas and can be written as $K = nR$, where n is the number of moles and R a new constant. In terms of this new constant we find,

$$\frac{PV}{T} = K(n) = nR \quad \text{or} \quad PV = nRT$$

The constant R has the value of PV/T for one mole of gas and is the same for all gases and is known as the *universal gas constant*.

To show that the constant R is not dependent on the kind of gas being studied, but is a constant universally applicable to all gases, we shall express $PV = nRT$ in the form $PV/RT = n$. If we take equal volumes of two gases at the same temperature and pressure, then, P, V and T for the two gases will have equal values. From Avogadro's principle, two gases at the same P, T and V will have the same number of moles, n. Therefore, it is necessary that R be the same for the two gases and similarly for all other gases.

The equation $PV = nRT$ is called the *ideal gas equation of state*; it tells us how the four variables (V, P, T and n) of an ideal gas are interrelated. The equation may be written as $PV/T = nR = $ CONSTANT (for a given amount of gas). We, therefore, have

$$P_1 V_1 / T_1 = P_2 V_2 / T_2 \quad (n \text{ is constant})$$

This equation is useful for calculating the volume V_2 of a gas under the arbitrary conditions of P_2 and T_2, from a knowledge of its volume V_1 at pressure P_1 and temperature T_1.

It is essential for every chemist to have a good understanding of the gas laws and to be able to apply them to a variety of problems in chemistry. There are some problems in which the use of the ideal gas law is not direct. Two important cases involve the determination of the density of a gas under given conditions and the evaluation of molecular mass from experimental data. These problems are readily treated if one expresses the law in terms of density and molecular mass and other measured quantities. We can write the ideal gas law as

$$P = nRT/V = gRT/VM = \rho RT/M$$

where g is the mass in grams, M the molecular mass and ρ the density.

6.7.1 The Gas Constant

Rearranging the equation of state, we find that $R = PV/nT$. The value of R is the value of PV/T for one mole of a gas. Since one mole of a gas occupies a volume of 22·414 litres at 1 atmosphere pressure and 273 K, we get,

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22 \cdot 414 \text{ litres}}{1 \text{ mol} \times 273 \text{ K}}$$

$$= 0 \cdot 0821 \frac{\text{litre atm}}{\text{mol K}}$$

If the pressure is written as force per unit area and the volume as area times length, we have

$$R = \frac{\dfrac{\text{FORCE}}{\text{AREA}} \times \text{AREA} \times \text{LENGTH}}{n \times T} = \frac{\text{FORCE} \times \text{LENGTH}}{n \times T}$$

The dimensions of force times length are those of work or energy. It follows that R has the dimensions of energy per degree per mole. Some of the more useful values of R are given in Table 6.3.

Table 6.3   Values of the Ideal Gas Constant R, in different Units

0·0821	litre-atm K⁻¹mol⁻¹	8·31 × 10⁷	erg K⁻¹mol⁻¹
82·1	ml-atm K⁻¹mol⁻¹	8·31	Joule K⁻¹mol⁻¹
62·3	litre-mm K⁻¹mol⁻¹	1·987	cal K⁻¹ mol⁻¹

Example 6.1 Given the volume of a gas as 200 ml at 800 mm pressure, calculate the volume of the same gas at 765 mm pressure, temperature being constant.

This problem is typical of many problems encountered with gases. The state of a gas is changed with one or more of its variables, T, P, V and n (or mass) remaining fixed. By writing the gas law for the two states, one can usually recognize the terms which are equal. Using this information and the given data one can calculate the unknown quantity.

In this problem for the gas in the two states we have

INITIAL STATE: $P_1 = 800$ mm; $V_1 = 200$ m; $n_1 = n$; $T_1 = T$; $P_1V_1 = nRT$

FINAL STATE: $P_2 = 765$ mm; $V_2 = ?$; $n_2 = n$; $T_2 = T$; $P_2V_2 = nRT$

Since both the temperature and amount of gas (n) are held constant, $P_1V_1 = P_2V_2$. Substituting numerical values

$$800 \text{ mm} \times 200 \text{ ml} = 765 \text{ mm} \times V_2$$

$$V_2 = \frac{800 \text{ mm} \times 200 \text{ ml}}{765 \text{ mm}} = 209 \text{ ml}$$

Example 6.2 A sample of 1·0 g of gas contained in a 1·0 litre vessel at 24°C exerts a pressure of 0·836 atm. What would be the pressure of the sample if it were compressed to a volume of 0·963 litre and heated to a temperature of 47°C.

For the gas in the two states we have
INITIAL STATE: $P_1 = 0\cdot836$ atm; $V_1 = 1\cdot0$ litre; $n_1 = n$; $T_1 = 273 + 24 = 297$ K; $P_1 V_1 = nRT_1$
FINAL STATE: $P_2 = ?$; $V_2 = 0\cdot963$ litre; $n_2 = n$; $T_2 = 273 + 47 = 320$ K; $P_2 V_2 = nRT_2$
In this problem nR is the same in the two states, therefore,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{or } P_2 = \frac{V_1}{V_2} \times \frac{T_2}{T_1} \times P_1$$

Substituting the numerical values

$$P_2 = \frac{1\cdot0 \text{ litre}}{0\cdot963 \text{ litre}} \times \frac{320 \text{ K}}{297 \text{ K}} \times 0\cdot836 \text{ atm} = 0\cdot935 \text{ atm}$$

Example 6.3 A helium-filled balloon is designed to rise to a height of 50 kilometres at which point it will be fully inflated and have the volume of one hundred thousand litres. At that altitude the temperature is −5°C and the atmospheric pressure is 1·52 mm. How many kilograms of helium will be needed to fully inflate the balloon?

To calculate the number of kilograms of helium required we shall first calculate the number of moles and then covert these to kilograms.

The balloon has flexible walls, hence the volume of the balloon varies with the applied pressure and at any height the pressure inside the balloon will be substantially equal to the atmospheric pressure. As the atmospheric pressure at a height of 50 km when the balloon is fully inflated is 1·52 mm, the pressure inside the ballon will also be 1·52 mm.

Hence for helium at a height of 50 km we have,

$P = 1\cdot52$ mm $\qquad\qquad n = ?$ $\qquad\qquad T = 273 - 5 = 268$ K

$V =$ Volume of balloon when fully inflated $\quad R = 0\cdot082 \dfrac{\text{litre atm}}{\text{mol K}} \quad n = PV/RT$

$\quad = 100,000 \text{ litres} = 1\cdot0 \times 10^5$ litres

Before substituting the given numerical values we have to see that the variables in the equation are expressed in the proper units. If we choose to use the value of R expressed in litre atm/mol K then the units of the terms in the equation are of necessity those that appear in R and any quantity or quantities which do not have those units must be converted before substituting in the gas law.

As R is in litre atm/mol K the pressure must be in atm, V in litres and T in Kelvin. Therefore, $P = 1\cdot52 \text{ mm} \times 1 \text{ atm}/760 = 2\cdot0 \times 10^{-3}$ atm; $V = 1\cdot0 \times 10^5$ litres and $T = 268$ K. Substituting the numerical values

$$n = \frac{PV}{RT} = \frac{2\cdot0 \times 10^{-3} \text{ atm} \times 1\cdot0 \times 10^5 \text{ litre}}{0\cdot0821 \dfrac{\text{litre atm}}{\text{mol K}} \times 268 \text{ K}}$$

$$= 9\cdot090 \text{ mol}$$

Since one mole of helium weighs 4 g, the mass of helium is $9\cdot09 \text{ mol} \times \dfrac{4\cdot00 \text{ g}}{1 \text{ mol}} = 36\cdot36$

$$g = 0\cdot03636 \text{ kilogram}$$

Example 6.4 A sample of gas weighing 5·75 g occupies a volume of 3·4 litres at 50° and 715 mm pressure. What is the molecular mass of the gas?

To solve this problem, we use the equation $P = gRT/VM$ or $M = gRT/PV$. In this problem, we

have $g=5\cdot75$ g; $R=0\cdot0821$ $\dfrac{\text{litre atm}}{\text{mol K}}$; $T=273+50=323$ K; and $P=715$ mm.

As R is litre atm/mol K, the pressure used must be in atm and V in litres.

$$P=715 \text{ mm}$$
$$=715 \text{ mm} \times \frac{1 \text{ atm}}{760 \text{ mm}} =715/760 \text{ atm}$$
$$V=3\cdot4 \text{ litres} \cdot$$

Substituting the values,

$$M = \frac{5\cdot75\text{g} \times 0\cdot0821 \dfrac{\text{litre atm}}{\text{mol K}} \times 323 \text{ K}}{\dfrac{715}{760} \text{atm} \times 3\cdot4 \text{ litres}}$$

$$=47\cdot7 \text{ g/mol}$$

Example 6.5 For the commercial production of chlorine one method uses the electrolysis of molten sodium chloride. The chemical reaction that occurs is

$$2\text{NaCl}(l) \rightarrow 2\text{Na}(l) + \text{Cl}_2(g)$$
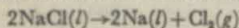
How many litres of chlorine will be produced from one kg of molten sodium chloride if the gas is measured at 27°C and 1 atm pressure?

From the chemical equation, it is apparent that for every 2 mole $(2 \times 58\cdot5=117\cdot0$ g$)$ of NaCl electrolysed, there will be formed 2 moles of sodium and one mole $(35\cdot5$ g$)$ of chlorine. This information can be written as

$$2 \text{ mol NaCl} \longrightarrow 1 \text{ mol Cl}_2$$
$$117 \text{ g NaCl} \longrightarrow 1 \text{ mol Cl}_2$$

Therefore,
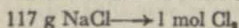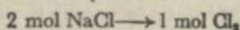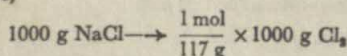
$$1000 \text{ g NaCl} \longrightarrow \frac{1 \text{ mol}}{117 \text{ g}} \times 1000 \text{ g Cl}_2$$
$$n=8\cdot55 \text{ mol Cl}_2$$

Assuming that chlorine obeys ideal gas law, $PV=nRT$, we have

$$V=nRT/P \qquad\qquad P=1 \text{ atm}$$
$$R=0\cdot0821 \frac{\text{litre atm}}{\text{mol K}} \qquad\qquad T=273+27=300 \text{ K}$$

Hence

$$V = \frac{8\cdot55 \text{ mol} \times 0\cdot082 \dfrac{1 \text{ litre atm}}{\text{mol K}} \times 300 \text{ K}}{1 \text{ atm}}$$

$$=2\cdot106 \times 10^2 \text{ litres}$$

6.8 MIXTURE OF GASES—DALTON'S LAW OF PARTIAL PRESSURES

So far we have considered the relation between P, V, T and n for a gaseous system in which only one component is present. If several substances are present in a gaseous mixture, we can still use the gas laws by taking into account the presence of different substances. The relationship between P, V, T and n in the mixture of gases can be illustrated by the experiment shown in Fig. 6.13. The three vessels are of equal volume and each has a manometer for measuring pressure of the gas. Let us pump a sample of nitrogen into a vessel (its pressure is found to be P_1 mm) and also a sample of oxygen into a second vessel

(and its pressure is found to be P_2 mm). Now if both the samples are pumped into a third vessel, the pressure here is observed to be the sum of P_1 and P_2. This shows that each component independently contributes to the total pressure.
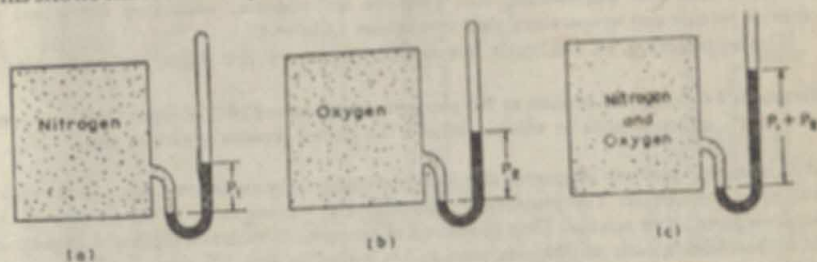
Fig. 6.13 Dalton's law of partial pressures

This behaviour of a mixture of two gases was first expressed in a generalised form in 1807 by John Dalton and is known as *Dalton's law of partial pressures*. This law states that the total pressure exerted by a mixture of non-reacting gases is equal to the sum of the pressures which each component would exert if placed separately in the container:

$$P_t = p_1 + p_2 + p_3 + \cdots \quad (T, V \text{ are constant})$$

where P_t is the total pressure and p_1, p_2, p_3, ... etc., are *partial pressures* of components 1, 2, 3, ... etc. In a concise form, we can write the above expression as

$$P_t = \sum_i p_i \quad (V \text{ and } T \text{ are constant})$$

where the symbol $\sum_i$ stands for the summation over all the components present in the mixture.

The partial pressure p_i of component i is defined as the pressure that the gas would exert if it were present alone in the same volume and at the same temperature. Thus, if a container of volume V contains n_1 moles of gas 1, n_2 moles of gas 2, and so on, then the partial pressures of gases 1, 2 and so on are,

$$p_1 = n_1 RT/V, \, p_2 = n_2 RT/V, \ldots$$

The total pressure of the system can be written as

$$P_t = \sum_i p_i = \frac{RT}{V} \sum_i n_i = n_t \frac{RT}{V}$$

where n_t is the total number of moles of gas present in the mixture, $n_t = n_1 + n_2 + n_3 + \cdots = \sum_i n_i$. This equation is an even more a general form of the ideal gas law, valid for mixtures as well as for pure gases; it combines in one equation the laws of Boyle, Charles, Avogadro, and Dalton.

For mixtures of gases, it is sometimes convenient to express the law of partial pressures in terms of mole fractions of the various components of the mixture. The mole fraction x_i of a component i is defined by, $x_i = n_i/n_t$, where n_i is the number of moles of component i and n_t is the total number of moles. The partial pressure p_i of component is then given by $p_i = x_i P_t$. Remember that $\sum_i x_i = 1$, so that $\sum_i P_i = P_t \sum_i x_i = P_t$.

A law similar to Dalton's law is *Amagat's law* of partial volumes. According to this law, $V_t = v_1 + v_2 + v_3 \ldots$, at constant temperature (T) and pressure (P). Here V_t represents the total volume and v_1, v_2, ..., the partial volumes.* Thus when two or more gases are mixed at constant volume and temperature, their pressures are additive; when they are mixed at constant pressure and temperature, their volumes are additive.†

The application of Dalton's law is illustrated by the following examples.

Example 6.6 A mixture of gases at 760 mm pressure contains 65·0% nitrogen, 15·0% oxygen and 20·0% carbon dioxide by volume. What is the partial pressure of each in mm?

A fundamental property of gases is that each component of a gas mixture occupies the entire volume of the mixture. The percentage composition by volume refers to the volume of the separate gases before mixing. Thus 65 volumes of nitrogen, 15 volumes oxygen and 20 volumes of carbon dioxide, each at 760 mm pressure are mixed to give 100 volumes of mixture at 760 mm.

For a mixture of ideal gases, Dalton's and Amagat's laws are equivalent. Therefore, in a gaseous mixture both the volume fraction v_i/V and the pressure fraction p_i/P of a component equal its mole fraction $x_i = n_i/n$.

Now as $p_i = \dfrac{v_i}{V}P$,

$$p_{N_2} = \frac{65}{100} \times 760 \text{ mm} = 494 \text{ mm}$$

$$p_{O_2} = \frac{15}{100} \times 760 \text{ mm} = 114 \text{ mm}$$

$$p_{CO_2} = \frac{20}{100} \times 760 \text{ mm} = 152 \text{ mm}$$

Total pressure $= p_{N_2} + p_{O_2} + p_{CO_2} = 760$ mm.

Dalton's law is put to practical use in laboratory work when the amount of gas evolved in a reaction is to be measured quantitatively. Often these gases are collected over water (Fig. 6.14a) It is a common practice to equalise the level of water inside and outside the gas-collecting bottle to make the pressure of the collected gas equal to the pressure of the atmosphere. This is done in order to measure the volume of gas at atmospheric pressure and temperature. If the gas were pure, one could immediately use the gas law to calculate the number of moles (or the quantity) of gas produced by the reaction. However, under the conditions of the experiment, the gas collected contains water vapour in addition to the gas of interest. Hence the pressure of the collected gas is *not* the atmospheric pressure (P_{atm}) even though equality of the liquid levels (Fig. 6.14b) indicates that the *total* internal pressure is equal to P_{atm}; for this total pressure, according to Dalton's law, is made up of the sum of the partial pressures of the gas in question (p_g) and the vapour pressure exerted by the liquid water (p_l) over which the gas is collected. Therefore, $P_{atm} = p_g + p_l$. Pressure of the water vapour is also known as *aqueous tension*. The pressure

*The partial volume v_i of component i is defined as the volume that the component would occupy if it were present alone at the same temperature (T) and at the same total pressure (P) of the mixture.

†Air is approximately 1/5 oxygen and 4/5 nitrogen by volume. This means that we might consider a sample of one litre of air measured at 1 atm as having been obtained by the mixing of 200 ml of oxygen and 800 ml of nitrogen, each at about 1 atm pressure. In the total of 1000 ml however this quantity of oxygen would exert a pressure of 1/5 of atm and the nitrogen 4/5 of 1 atm. We might also think of the mixture as consisting of 1000 ml of oxygen at a partial pressure of 1/5 atm and 1000 ml nitrogen at a partial pressure of 4/5 atm. Thus, partial pressures of the gases in the mixture are proportional to their volumes when both are measured at the same pressure.

Reaction mixture
Producing gas

Pneumatic trough
(a)

(b)
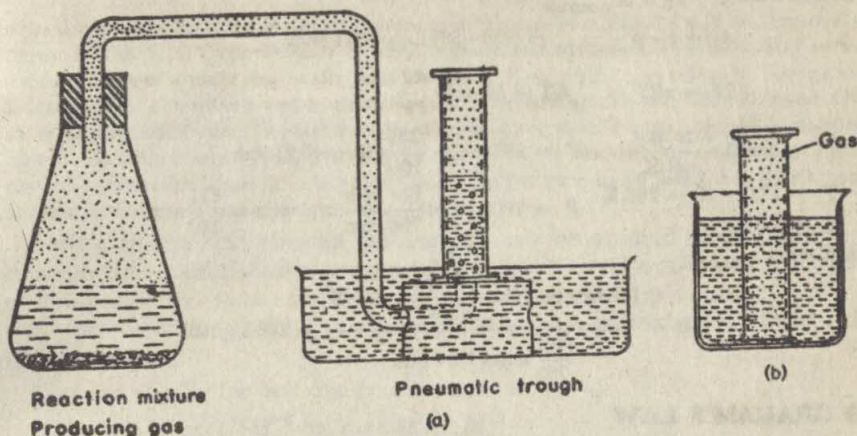
Fig. 6.14 (a) Collection of a gas over water. (b) The water inside the vessel is at the same level as it is outside. Although the pressure inside the vessel equals the atmosphereic pressure, the pressure of the collected gas is not equal to the atmospheric pressure because the gas contains water molecules as well as the molecules of the gas in question.

of water vapour is dependent on temperature and its values at different temperatures may be found in reference tables. Whenever a gas is collected over water the pressure of the gas is obtained by subtracting the aqueous tension from the atmospheric pressure (recorded by barometer).

Example 6.7 A sample of oxygen is collected by displacing water from an inverted tube. The temperature is 25°C, the pressure is 750 mm (barometric pressure) and the volume occupied is 280 cc. What is the true volume of oxygen at STP? (Aqueous tension at 25°C=23·8 mm)

As the gas is collected over water the barometer pressure (P_{bar}) does not correspond to the actual pressure of the gas

$$P_{bar} = p_{O_2} + p_{H_2O}$$

$$p_{O_2} = P_{bar} - p_{H_2O}$$

$$= (750 \cdot 0 - 23 \cdot 8) \text{ mm} = 726 \cdot 2 \text{ mm}$$

Volume of gas at STP can be calculated as:

INITIAL STATE: $P_1 = 726 \cdot 2$ mm ; $V_1 = 280$ cc; $n_1 = n$; $T_1 = 273 + 25 = 298$ K; $P_1 V_1 = nRT_1$

FINAL STATE: $P_1 = 760$ mm; $V_2 = ?$; $n_2 = n$; $T_2 = 273$; $P_2 V_2 = nRT_2$

As nR is the same in the two states,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1}{P_2} \times \frac{T_2}{T_1} \times V_1$$

$$= \frac{726 \cdot 2 \text{ mm}}{760 \text{ mm}} \times \frac{273 \text{ K}}{298 \text{ K}} \times 280 \text{ cc} = 245 \text{ cc}$$

Example 6.8 250 cc of a gas is collected over acetone at −10°C and 85 cm. If the gas weighs 1·34 g and the vapour pressure of acetone at −10° is 39 mm, what is the molecular mass of the gas?

By Dalton's law $P = p_g + p_{acetone}$ or

$$p_g = P - p_{acetone} = (850-39) \text{ mm} = 811 \text{ mm}$$

$$PV = nRT = \frac{g}{M}RT \text{ or } M = g \cdot \frac{RT}{PV}$$

$R = 0.0821 \dfrac{\text{litre atm}}{\text{mol K}}$ $V = 250 \text{ cc} = \dfrac{250}{1000} \text{ litre} = 0.25 \text{ litre}$

$T = 273 - 10 = 263 \text{ K}$ $P = 811 \text{ mm} = \dfrac{811 \text{ mm}}{760 \text{ mm}} \times 1 \text{ atm} = \dfrac{811}{760} \text{ atm}$

$g = 1.34 \text{ g}$

Substituting,

$$M = \frac{1.34 \text{ g} \times 0.0821 \dfrac{\text{litre atm}}{\text{mol K}} \times 263 \text{ K}}{\dfrac{811}{760} \text{ atm} \times 0.25 \text{ litre}} = 108.5 \text{ g/mol}$$

6.9 GRAHAM'S LAW

Gases have a remarkable tendency to occupy all the space available to them. When a small quantity of hydrogen sulphide gas is released in a laboratory its smell spreads because the gas diffuses through the atmosphere and distributes itself throughout the room. This property of a gas which involves the movement of the gas molecules through gases of another kind is called *diffusion*. When a gas (under pressure) is allowed to escape from a container (effuse) through a very small opening as shown in Fig. 6.15, the phenomenon is called *effusion*.
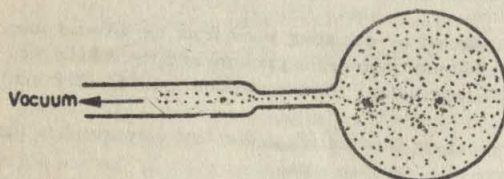
Fig. 6.15 Effusion of a gas through a pinhole into a vacuum

$$NH_{3(g)} + HCl_{(g)} = NH_4Cl_{(s)}$$
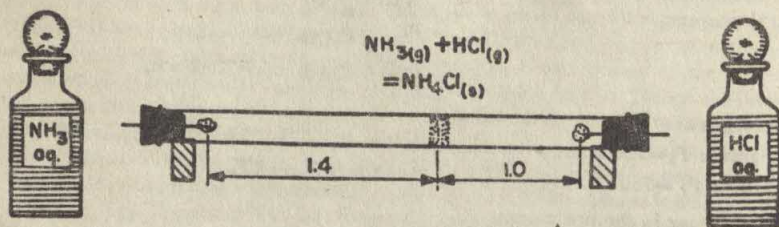
Fig. 6.16 Apparatus for demonstrating diffusion phenomenon. When two cotton plugs, one soaked in concentrated aqueous ammonia and the other in concentrated hydrochloric acid are placed at opposite ends of a closed tube, a ring of solid ammonium chloride dust eventually forms where the ammonia molecules meet the hydrogen chloride molecules on the hydrogen chloride side of the tube. Ammonia molecules, on the average, move 1.4 times as far as the hydrogen chloride molecules. Hence, on the average, the ammonia molecules must have a velocity 1.4 times greater than of the hydrogen chloride molecules.

Diffusion phenomenon may easily be illustrated with the help of an experiment as described in Fig. 6.16. Introduce simultaneously two cotton plugs, one soaked in concentrated hydro-

chloric acid and the other in liquor ammonia at the ends of a glass tube (1 cm diameter) as shown in Fig. 6.16. Close the ends by cork to prevent air draughts. In a short time we find the formation of a white ring in the tube at a place closer to the end where HCl cotton wad is introduced. The white cloud is ammonium chloride which is formed when HCl and NH_3 move towards each other. The fact that the cloud is nearer to HCl implies that HCl molecules moved relatively slowly. We know that a molecule of HCl is heavier compared to that of NH_3 molecule. From this it may be concluded that the lighter gases move faster than heavier gases under identical conditions of temperature and pressure.

Both diffusion and effusion phenomena can be studied under controlled experimental conditions and are described quantitatively by *Graham's law* which states, under the same conditions of temperature and pressure the rate of diffusion (or effusion) of a gas is inversely proportional to the square root of its molecular mass.

Mathematically the law can be expressed as

$$r \propto 1/(M)^{\frac{1}{2}} \text{ or, } r = \text{CONST}/(M)^{\frac{1}{2}}$$

$$r_1/r_2 = (M_2/M_1)^{\frac{1}{2}}$$

where r_1 and r_2 are the rates of diffusion of gases 1 and 2, and M_1 and M_2 are their respective molecular masses. Since it is rather difficult to deal with absolute rates of diffusion of gases, attention is usually confined to the relative rate of diffusion of gases. The law is useful for the determination of molecular masses of gases. It should, however, be remembered that this law is true only for gases diffusing under low pressure.

Example 6.9 The speeds of diffusion of CO_2 and O_2 were found to be 0·29 and 0·271. What is the molecular mass of O_2 if the molecular mass of CO_2 is 44.

$$\frac{r_{O_2}}{r_{CO_2}} = \left(\frac{M_{CO_2}}{M_{O_2}}\right)^{\frac{1}{2}}, \text{ i.e. } \frac{0\cdot271}{0\cdot29} = \left(\frac{44}{M_{O_2}}\right)^{\frac{1}{2}}$$

Squaring both sides,

$$\frac{(0\cdot271)^2}{(0\cdot29)^2} = \frac{44}{M_{O_2}}$$

or

$$M_{O_2} = 44 \times \frac{(0\cdot29)^2}{(0\cdot271)^2}$$

$$= \frac{44 \times 0\cdot29 \times 0\cdot29}{0\cdot271 \times 0\cdot271} = 50\cdot4$$

Molecular mass of $O_2 = 50\cdot4$

6.10 KINETIC MOLECULAR GAS MODEL

In the preceding sections of this chapter, we examined the physical behaviour of gases from an empirical point of view and paid no attention to questions like why gases occupy the entire space available to them, why they are highly compressible, how gases exert pressure, why different gases diffuse at different rates, and so on. Since it is not possible to deduce the nature of gases from the measured properties alone, it becomes necessary to look for a model to account for the observed facts. In order that the model be simple, certain assumptions will have to be made about the nature of gases. We shall now examine such a model first by discussing the validity of assumptions and later by comparing its predictions with observed facts.

6.10.1 Assumptions of Kinetic Theory

The following assumptions are made to describe an ideal gas.

(*i*) A gas consists of a large number of particles (atoms or molecules) that are so small and so far apart (on the average) that the actual volume of the molecules is negligible compared to the empty space between them. This assumption seems to be justified in view of the great compressibility of the gas. Calculations (see Example 6.10) also show that about 99·9 per cent of the total volume in nitrogen gas at STP is not occupied by molecules. The average spacing between molecules of nitrogen at STP is worked out to be about ten times the molecular diameter. When the gas is compressed, the average spacing between molecules is reduced.

(*ii*) There are no attractive forces between molecules and the molecules are completely independent of one another. The support for this assumption comes from the observation that even highly compressed gases expand spontaneously to occupy all the space available. This suggests that there is no appreciable interaction between molecules.

(*iii*) The molecules of a gas move randomly in straight lines colliding with one other and also with the walls of the container. The pressure exerted by a gas is the result of collisions of the molecules with the walls of the container. That particles of a gas are not at rest but in a state of continuous motion (called thermal agitation) cannot be directly observed because molecules are too small to be seen individually even through the best microscope. However, movement of particles of size in the neighbourhood of 1 micron (10^{-4} cm) diameter (e.g. particles of smoke floating in air) can be observed microscopically. This phenomenon is called *Brownian motion* (after the British botanist who first observed the irregular motion of pollen particles suspended in water). In Fig. 6.17, we show the successive positions of a smoke particle performing Brownian motion in air. It is found that the smaller the particles, the more violent is the irregular motion; also, the higher the temperature, the more vigorous is the movement of the particles. In the absence of attractive forces between molecules,
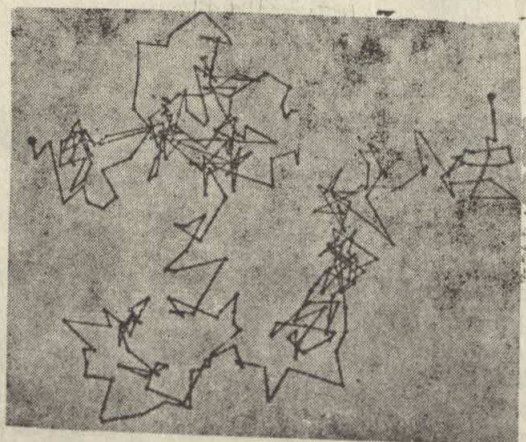
Fig. 6.17 Brownian motion. The successive positions of a smoke particle in the air recorded at one minute intervals.

it is reasonable to assume straight line random motion for the molecules which are much smaller in size than the smoke particles. Molecules, however, change their path as a result of collision with other molecules or the walls of the container.

(*iv*) In these collisions, there is no net loss of kinetic energy, although, there may be a transfer of energy between the partners in the collisions (i.e. the collisions are elastic). If there were loss of kinetic energy in collisions (inelastic collisions), the motion of molecules would eventually stop and the pressure and temperature would drop to zero. Since the pressure of a confined gas does not change with time (unless we heat or cool it), we conclude that a gas exerts pressure through elastic collisions with the wall.

(*v*) At any particular instant, different molecules in a sample of gas have different speeds and hence different kinetic energies, but the average kinetic energy of a molecule is directly proportional to the absolute temperature. The assumption that at any instant different molecules have different speeds and hence different energies is valid in view of the great number of molecular collisions. As molecules collide with each other, we would expect the speed of the molecules to change. All the molecules in a container will, therefore, not have the same speed at any one time. Even if the molecules had the same initial speed, the effects of collisions would soon disrupt such uniformity. The speed of each gaseous molecule probably changes billions of times during a second and we have no way of knowing the speed or kinetic energy of each individual molecule. Instead, we shall make a statistical approach to predict as to how many of the molecules have a particular speed and kinetic energy. We shall now examine the distribution of moleculear speeds briefly.

In order to understand the distribution of molecular speeds, it may be helpful to look at a familiar distribution. As an example, we consider the distribution of performance of students in a class test. Let us suppose that there are 100 students and we have information about the marks (percentage-wise) obtained by each student. It is difficult to obtain a reasonably

Table 6.4

Marks (%)	No. of students
10–20	1
20–30	4
30–40	10
40–50	20
50–60	40
60–70	20
70–80	5
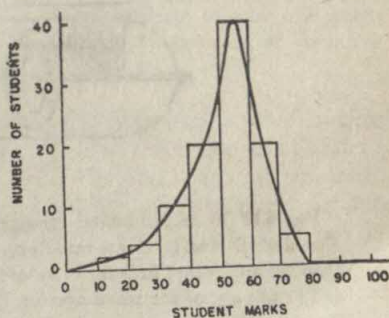
Fig. 6.18 Statistical distribution of student marks

accurate idea of how the marks are distributed among the students by looking at the marks of each student.* For the purpose of obtaining a better idea of how the marks are distributed in the class we study the performance distribution of the students by grouping together all students with marks within a certain range. Let this be 10. Then all students having marks ranging between, say 10–20%, 20–30%, etc., will be grouped together as shown in Table 6.4,

*The situation becomes much more complicated if the number is large.

and plotted in Fig. 6.18. It is obvious that not all the students have the same marks and the students in the class are ' distributed ' over this range of marks. The height of each rectangle in Fig. 6·18 refers to the number of students having marks within the range indicated by the base of the rectangle.

A more precise distribution can be obtained if a smaller value of ' marks range ' is adopted and the corresponding distribution determined. If the range is very small, and the number is very large, we have an outline like the smooth curve given in the figure.

In the case of gases, Maxwell and Boltzmann independently predicted theoretically the shape of the distribution curve of molecular speeds in a sample of gas at a given temperature (*Maxwell–Boltzmann Distribution Law*), assuming

(a)
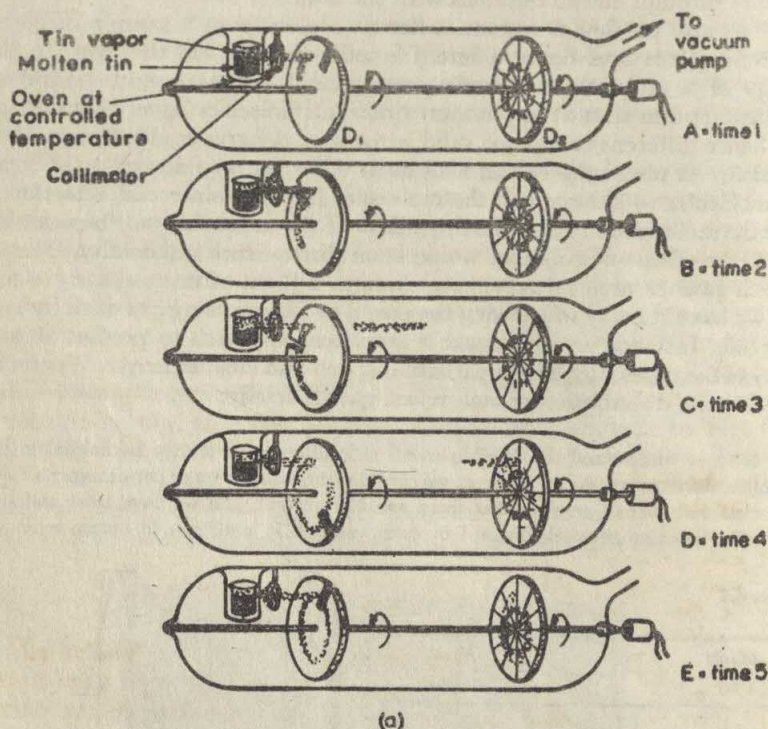
Fig. 6.19 (*a*) Experimental arrangement for measurement of molecular speeds. Two discs D_1 and D_2 rotate rapidly on the same axle. These discs are in an evacuated chamber and rotate in front of an oven containing molten tin. Some tin vapourises and steams out of the small opening in the oven, striking the first rotating disc, D_1. Once during every rotation the slot in this disc is in line with the hole of the oven. Then a small sample of tin molecules can pass through the slot and move on towards the second disc, D_2. The fast moving molecules lead the way. Slower moving molecules begin to lag behind. As the molecules reach the second disc they condense on it. Since this disc also is rotating, fast moving molecules would condense on sections *B*, *C* and *D*. Slow-moving molecules take a longer time to reach the second disc. The speed of the rotating disc is adjusted so that the slowest molecules condense on sections *I*, *J* and *K*. Many different groups of tin molecules pass through the first rotating disc each second. Soon a layer of metallic tin builds up on the second disc. The amount of tin in each of the sections *A* through *L* can be determined.
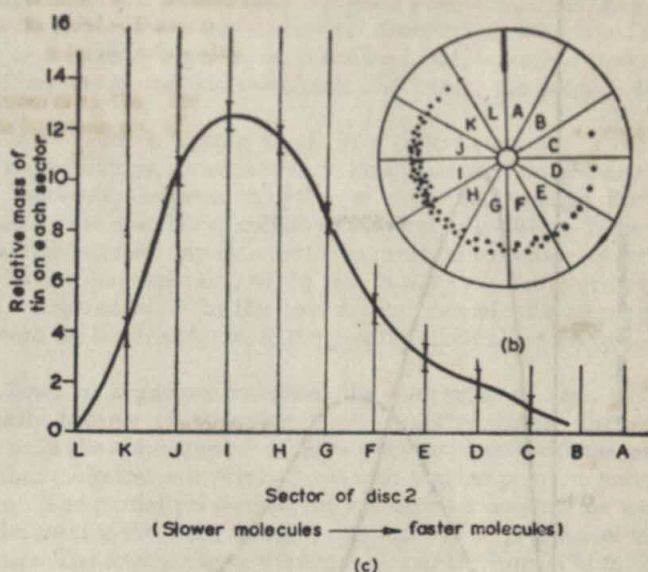
Fig. 6.19 (*b*) and (*c*) The results of an experiment with apparatus shown in (*a*) are shown in (*b*) (inset). The largest amount of tin is found on section *I*. In our illustrative experiment, no tin is deposited on the first or last sections *A* and *L*. From such a disc, the distribution curve shown in Fig. 6.19(*c*) can be derived.

We can also calculate approximately the fraction of the molecules having a particular speed (u_0). To do this we must know how far apart the discs are and how fast they rotate. We can then plot the fraction of the tin molecules having velocity v_0 versus molecular speed. Strictly speaking we cannot talk of the speed of a molecule because of the statistical nature of the distribution of molecular speed; what we can say is this much fraction of molecules has speed centered around u, i.e. their speeds lie in the region $u \pm \Delta u$.

that the molecular collisions are completely random and involve all possible values for the exchange of kinetic energy. It is only the total kinetic energy of a gas but not individual kinetic energies of molecules, that stays constant at a fixed temperature. Fig. 6.19(*a*) shows an experimental arrangement for obtaining data on molecular speeds. The data obtained from such experiments fit the theoretical curves within the limit of experimental errors (Fig. 6.19*c*). This experiment can be repeated at different temperatures and the distribution curves for tin molecules at 500 K and 1500 K are shown in Fig. 6.20. There is a larger fraction of fast moving molecules at higher temperature. The peaks in the distribution curves tell us that the largest fraction of molecules have speed of about 2×10^4 cm/s at 500 K and about 4×10^4 cm/s at 1500 K. Table 6.5 gives some numerical values of molecular speeds for different gases and different temperatures. The distribution curve tells us what fraction of the molecules have a particular speed. We see that only a small fraction of the molecules have very low (close to zero) or very high speeds; most of the molecules have intermediate speeds. The kinetic energy of a molecule is $\frac{1}{2} mu^2$, hence the **speed distribution can be converted into an energy distribution.**

16
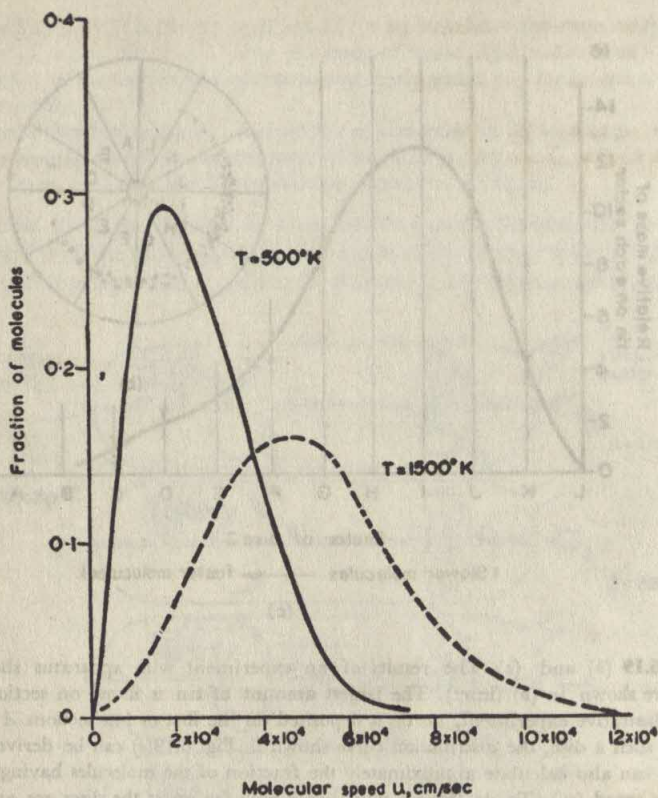
Fig. 6.20 Molecular speed distribution for tin at two temperatures

The assumptions of the kinetic theory made above, satisfactorily account for the observed behaviour of gases.

Boyle's law: We have assumed that a gas exerts pressure as a result of collision of the molecules on the walls of the vessel. The magnitude of the pressure would therefore depend on the frequency of collisions which in turn depends on the number of molecules and their average speed. When the amount of gas and temperature are constant, the number of molecules and the average speed remain constant. If the volume is reduced, the molecules do not have much

Table 6.5 Molecular Speeds[1]

Molecule	Temperature K	Average speed cm/s	Molecule	Temperature K	Average speed cm/s
H_2	273	18×10^4	N_2	273	4.9×10^4
H_2	1500	42×10^4	CO_2	273	3.9×10^4
O_2	273	4.6×10^4			

[1]Escape velocity from earth's gravitational field is about 11 kilometre/s.

space to move and hence collide with the walls more frequently. As a result of this, the walls receive more impacts and the observed pressure would therefore be greater in a small volume. If, on the other hand, volume is increased, the number of impacts on the walls decreases and hence, the pressure decreases.

Charles' law: When a sample of gas in a closed container is heated, the molecules receive energy, move faster and hit the walls of the container harder and more frequently, the pressure of the gas, therefore, increases. Pressure is a result of two factors: number of collisions and force of collisions. If the pressure is not allowed to increase, any increase in temperature will cause (in accordance with Charles' law) an expansion of the gas. In this case, the increased force of collisions is compensated for by the decreased number of collisions per unit area resulting from the larger volume, so the pressure remains unchanged.

Dalton's law: In a gaseous mixture, the molecules of each gas behave independently because of the absence of attractive forces. Each molecule strikes the walls the same number of times per second and with the same force as if no other molecules are present, provided the temperature and pressure are constant. The partial pressure of the gas depends only on the number of its molecules striking the walls and is unaffected by the presence of molecules of other gases. The total pressure exerted is due to the impact of molecules of all the gases present in the mixture.

Graham's law: This law follows from the assumption that the average kinetic energy of molecules is fixed for a given temperature. This means at the same temperature, the average kinetic energy of molecules of one gas is equal to the average kinetic energy of molecules of another gas. If m_1 and m_2 are the masses and u_1 and u_2 are the average speeds of gases 1 and 2, then

$$\tfrac{1}{2}m_1 u_1^2 = \tfrac{1}{2}m_2 u_2^2$$
$$\text{or } u_1^2/u_2^2 = (m_2/m_1)$$
$$\text{or } u_1/u_2 = (m_2/m_1)^{1/2}$$

If we assume that the rates of diffusion are directly proportional to the average speeds of their molecules, we may write

$$\frac{\text{RATE OF DIFFUSION OF GAS 1}}{\text{RATE OF DIFFUSION OF GAS 2}} = \frac{r_1}{r_2} = \left(\frac{m_2}{m_1}\right)^{1/2} = \left(\frac{m_2 N_0}{m_1 N_0}\right)^{1/2} = \left(\frac{M_1}{M_2}\right)^{1/2}$$

This is Graham's law of diffusion.

Example 6.10 (*i*) What is the average volume available to a molecule in a sample of nitrogen gas at STP? (*ii*) Assuming that N_2 molecule is approximately spherical with an effective diameter of 3·6 A, calculate

   (*a*) the actual volume occupied by a N_2 molecule;

   (*b*) the percentage of the molar volume that is empty space; and

   (*c*) the average distance between neighbouring gas molecules at STP.

(*i*) We know that one mole of an ideal gas at STP (i.e. at 0°C and 1 atm pressure) occupies 22·4 litres. Therefore assuming ideal behaviour for nitrogen, one mole of this gas will occupy 22·4 litres or 22,400 cm at 0°C and 1 atm pressure.

There are $6·02 \times 10^{23}$ molecules in one mole. Therefore the number of molecules in 1 cc is

$$\frac{6·02 \times 10^{23}}{22,400} = 2·69 \times 10^{19} \text{ molecules per cc}$$

and the volume available to a gas molecule is

$$\frac{1}{2.69 \times 10^{19}} = 3.72 \times 10^{-20} \text{ cc molecule}^{-1}$$

(ii) Volume of a sphere $= (4/3)\ \pi\ r^3$

As diameter for nitrogen is $3.6\text{A} = 3.6 \times 10^{-8}$ cm

$$r = \text{radius of nitrogen molecule} = \frac{3.6 \times 10^{-8}}{2} \text{ cm} = 1.8 \times 10^{-8} \text{ cm}$$

Volume of a nitrogen molecule $= 4/3\pi(1.8 \times 10^{-8})^3$
$$= 2.44 \times 10^{-23} \text{ cc molecule}^{-1}$$

Volume of 1 mole of nitrogen molecules
$$= 2.44 \times 10^{-23} \times 6.20 \times 10^{23} = 14.7 \text{ cc mol}^{-1}$$

We find that the actual volume occupied by 1 mole of molecules is 14·7 cc while the gas molar volume is 224,00 cc. Thus the difference $224,00 - 14.7 = 223,85.3$ cc is is apparently empty space.

$$\text{PER CENT EMPTY SPACE} = \frac{\text{VOLUME EMPTY}}{\text{VOLUME AVAILABLE}} \times 100$$

$$= \frac{223,85.3}{224,00} \times 100 = 99.9\%$$

The average distance between any molecule and its nearest neighbour can be obtained from the volume available to a gas molecule. Let us assume that the volume available to a molecule has the shape of sphere of radius R.* Hence the volume available to a molecule is $(4/3)\pi R^3$ and this is equal to 3.72×10^{-20} cc as found in (i).

$$(4/3)\pi R^3 = 3.72 \times 10^{-20} \text{ cc}$$

$$R^3 = \frac{3 \times 3.72 \times 10^{-20}}{4 \times \pi} \text{ cc}$$

$$R = 20.7 \times 10^{-8} \text{ cm}$$

Thus, on an average, the volume available to a gas molecule, can be assumed to be the volume of a sphere with $R = 20.7 \times 10^{-8}$ cm, and accordingly the average distance between the centres of any two neighbouring molecules in the gas sample will be $2R$. Therefore the average distance between a gas molecule and its nearest neighbour is $2R = 2 \times 20.7 \times 10^{-8} = 41.4 \times 10^{-8}$cm $= 41.4$ A.

Note that these calculations are approximate and give only a rough idea about the magnitude of the distance between the gas molecules in a sample of gas.

Another way of computing the distance between a gas molecule and its nearest neighbour in a sample of gas is by assuming that the gas volume is divided into small cubes of edge-length l and the volume of this small cube is the volume, on an average, available to a gas molecule. The length of this small cube (l) will then roughly be equal to the average distance between the gas molecules.† If l^3 is the volume of each small cube, then the value of l can be computed from the relation

$$l^3 = 3.72 \times 10^{-20} \text{ cc}$$

where 3.72×10^{-20} is the volume available to each molecule

or $l = 33.4 \times 10^{-8}$ cm $= 33.4$ A

From these calculations, we find that the average distance between two neighbouring molecules at STP is about 33.4×10^{-8} cm or 33·4 A. (Students should find out why this value is different from that obtained previously.) The diameter of the gas molecule is only 3·6 A and the distance between molecules in the gas is, therefore, about ten times their diameter.

Similar calculations for solid (density 1·03 g/cc) and liquid (density 0·8 g/cc) nitrogen show that in these states, the average distance between molecules is about 3·56 A and 3·8 A res-

*Not to be confused with r which represents the effective radius of the molecule.

†Here we are assuming that the molecules are for most part evenly spaced at the centres of identical cubes.

pectively (which are nearly equal to the molecule diameter of nitrogen). Hence in solid or liquid states, individual molecules touch each other and it is difficult to compress the substance in these states unlike in the gaseous state.

6.10.2 Pressure and Temperature of Gases as Derived from Kinetic Theory

Making use of the postulates of the kinetic molecular theory described earlier we can derive the following expression for the pressure of a gas in terms of the speed of molecules:

$$PV = \tfrac{1}{3} Nm <u^2>$$

where $<u^2>$ is the mean square speed of all the molecules in a given gas. The derivation of this relation is detailed below. We note here that if a system consists of N molecules of gas with n_1 molecules with speed u_1, n_2 molecules with speed u_2, ... and so on, the mean square speed of all the molecules in the gas is defined as

$$<u^2> = \frac{n_1 u^2_1 + n_2 u^2_2 + n_3 u^2_3 + \cdots}{N} = \sum_i \frac{n_i u^2_i}{N}$$
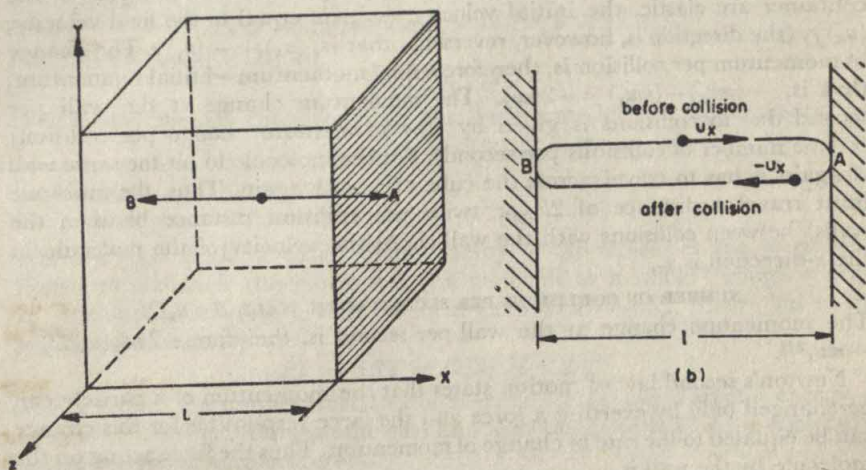
Fig. 6.21 (*a*) Molecular collision in a cube in the *X*-direction. (*b*) (i) Change in momentum per collision = final momentum − initial momentum = $-mu_x - (mu_x) = -2mu_x$

(ii) Since the wall *A* receives a collision each time the particle travels the box length *l* and back, that is, a round trip of distance $2l$, distance travelled by the particle between two successive collisions on wall $A = 2l$. The time Δt between successive collisions with wall *A*,

$$\Delta t = \frac{\text{DISTANCE TRAVELLED BY THE PARTICLE PER ROUND TRIP}}{\text{PARTICLE VELOCITY}} = 2l/u_x.$$

Number of collisions the particle makes with wall *A* per second, $1/\Delta t = u_x/2l$.

= momentum change per collision × number of collisions per second = $(-2mu_x) \times \left(\dfrac{u_x}{2l}\right)$

$$= -mu_x^2/l = F_w$$

F_w is the force exerted on the molecule by the wall. This is equal to $-F_x$ which is the force exerted by the molecule on the wall. Note that pressure is force exerted per unit area by the molecules on the wall.

Let us imagine a definite mass of gas contained in a cubical vessel. The stipulation of cubic container is not necessary, but it simplifies the derivation. Let the length of the cube edge be 1 cm, the number of molecules present in the cube be N, the mass of each molecule be m grams and the velocity of a molecule be u cm/s (molecules can move in all directions with different speeds). Velocity, u, is a vector quantity (having both magnitude and direction) and it can be resolved into three components, u_x, u_y and u_z mutually perpendicular to each other and parallel to the edges of the cube (Fig. 6.21a).

Let us now consider the effect of the x-component of velocity of a molecule. As a result of this velocity component in the x-direction, the molecule will collide with one wall of the container which is perpendicular to the X-axis, then bounce back and subsequently collide with the opposite wall (Fig. 6.21b). It is the total effect of such impacts with the walls of the container that produces the gas pressure.

When the molecule collides with the wall A and its direction is reversed, it exerts a force (F_x) on the wall and the wall exerts an equal and opposite force (F_w) on the molecule resulting in the reversal of the direction of motion of the particle. If we assume that the collisions of the particle with the walls of the container are elastic, the initial velocity, $(u_x)_i$, is equal to the final velocity, $(u_x)_f$, (the direction is, however, reversed), that is, $(u_x)_i = -(u_x)_f$. The change of momentum per collision is, therefore = final momentum − initial momentum, that is, $-(mu_x) - (mu_x) = -2mu_x$. The momentum change at the wall per second due to collisions is given by (the momentum change per collision) × (the number of collisions per second). For the molecule to hit the same wall A again it has to travel across the cube and back again. Thus, the molecule must travel a distance of $2l$ (or twice the collision distance between the walls) between collisions with the wall A. As the velocity of the molecule in the x-direction is u_x,

NUMBER OF COLLISIONS PER SECOND WITH WALL $A = u_x/2l$

The momentum change at the wall per second is, therefore, $-2mu_x(u_x/2l) = -mu_x^2/l$.

Newton's second law of motion states that the momentum of a particle can be changed only by exerting a force and the force responsible for this change can be equated to the rate of change of momentum. Thus the force acting on the molecule by the wall is,

$$F_w = -mu_x^2/l$$

The force exerted on the wall by the particle (F_x) is equal in magnitude, but opposite in sign to F_w; therefore,

FORCE EXERTED BY THE MOLECULE ON WALL, $F_x = -F_w = mu_x^2/l$

Now there are N molecules in the box, each having mass m. Each of these molecules may have different values of velocity in the x-direction. Let u_{x1}, u_{x2}, $u_{x3} \ldots u_{xi}$ represent the x-component of the velocity of molecule 1, 2, $\ldots$ and so on. The total force on wall A by the N molecules is the sum of the forces due to individual molecules.

$$F_x = \frac{m}{l}(u^2_{x1} + u^2_{x2} + u^2_{x3} + \ldots u^2_{xi}) = \frac{m}{l}\sum_i u^2_{xi}$$

Multiplied and divided by N, the number of molecules, the equation yields

$$F_x = \frac{Nm}{l}\sum_i \frac{u^2_{xi}}{N} = \frac{Nm}{l}<u^2_x>$$

where $<u^2{}_x> = \sum_i u^2{}_{xi}/N$ is the average value of the square of the x-component of the velocities.

Since pressure is defined as force per unit area, the pressure on wall A, having area l^2 is given by,

$$P_x = \frac{F_x}{l^2} = \frac{Nm<u^2{}_x>}{l^3} = \frac{Nm<u^2{}_x>}{V}$$

where V is the volume of the box. The pressure P exerted by a confined gas is the same in all directions. Therefore, the pressure on the wall A, P_x, is also the pressure on all the other walls of the cube. Thus, we can write,

$$P = P_x = \frac{Nm<u^2{}_x>}{V}$$

Since the molecular motion is random (there is no preference to any one direction), the average values of the square of the component velocities in the three mutually perpendicular directions must be equal, i.e.

$$<u^2{}_x> = <u^2{}_y> = <u^2{}_z>$$

Since the velocity u is related to its three velocity-components by the relation, $u^2 = u^2{}_x + u^2{}_y + u^2{}_z$ it follows that

$$<u^2> = <u^2{}_x> + <u^2{}_y> + <u^2{}_z> = 3<u^2{}_x>$$

We, therefore, obtain the relation,

$$PV = \tfrac{1}{3}Nm<u^2>$$

The fundamental equation from the kinetic model can be expressed as,

$$PV = (1/3) \, Nm<u^2> = (2/3) \, N \, (1/2) \, m<u^2>$$

Recalling that kinetic energy is $1/2 \, mu^2$,

$$PV = (2/3) \, N <\text{KE}>$$

where $<\text{KE}>$ is the average kinetic energy of the molecules due to translations (translation is the movement of a molecule as a whole through space). If we compare this result with the ideal gas law $PV = nRT$ we are led to the important identification

$$PV = nRT = (2/3) \, N <\text{KE}>$$

which relates the temperature to the average translational kinetic energy of the molecules (that compose the gas) and provides us with a kinetic molecular interpretation of temperature.

Since $nRT = (2/3) \, N <\text{KE}>$, we have $<\text{KE}> = (3/2) \, (n/N)RT$. Now the number of moles, n and the number of molecules, N, are related by, $n = N/N_0$, where N_0 is the Avogadro's number. Thus,

$$<\text{KE}> = \tfrac{3}{2} \frac{N}{N_0} \frac{RT}{N} = \tfrac{3}{2} \frac{R}{N_0} T = \tfrac{3}{2} kT$$

The constant $k = R/N_0 = 1 \cdot 381 \times 10^{-16}$ erg molecule^{-1} K^{-1} is called the *Boltzmann constant*. The above equation defines absolute temperature in terms of the translational kinetic energy of an ideal gas.

The definition of temperature

$$T = \frac{2}{3k} (\tfrac{1}{2} \, m<u^2>) = \frac{2}{3k} <\text{KE}>$$

obtained from the kinetic theory now provides us with a natural zero for a temperature from microscopic point of view. When the average kinetic energy of the molecules of the gas is zero, that is, the random or chaotic motion,

often called the thermal motion of the molecules, has come to a complete standstill, the temperature is at absolute zero.*

Note that at any temperature the average kinetic energy of the molecule in a gas is

$$<\text{KE}> = (1/2)m <u^2> = (3/2) kT;$$

therefore $<u^2> = 3kT/m = 3RT/M$,

where $M = mN_0 =$ molecular mass of the gas; or

$$(<u^2>)^{\frac{1}{2}} = (3RT/M)^{\frac{1}{2}}$$

The quantity $(<u^2>)^{\frac{1}{2}}$ is called the root-mean-square speed (u_{rms}). The average molecular speed $<u>$ is given by the expression

$$<u> = \frac{\Sigma n_i u_i}{N} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = 0.9213 \, u_{rms}$$

But we shall not derive this here.

Example 6.11 Calculate the kinetic energy of an Avogadro number of gas molecules at 0°C.

Kinetic energy of an Avogadro number of molecules

$$<\overline{\text{KE}}> = N_0 <\text{KE}> = N_0 (3/2) kT = (3/2) RT$$

The value of R is 1.987 cal mol^{-1} K^{-1}, and $T = 273$ K. Thus, the kinetic energy of one Avogadro number of molecules

$$= (3/2) \times 1.987 \text{ cal/mol K} \times 273 \text{ K} = 814 \text{ cal mol}^{-1}$$

Note that in this calculation, the nature of gas molecules is unimportant. All ideal gases at 0°C will have this amount of kinetic energy.

The average kinetic energy of a gas molecule $<\text{KE}>$ is generally expressed in ergs and not in calories and at 0°C, it has the value

$$<\text{KE}> = \tfrac{3}{2} kT$$
$$= \tfrac{3}{2} \times 1.381 \times 10^{-16} \text{ erg/molecule K} \times 273 \text{ K}$$
$$= 5.66 \times 10^{-14} \text{ erg/molecule}$$

Example 6.12 Calculate the root-mean-square speed of oxygen molecules in the lungs at normal body temperature 37°C.

$$u_{rms} = (3RT/M)^{1/2}$$

In order to give u_{rms} the units of cm/s, the value of R must be expressed in mechanical energy units, i.e. in ergs (1 erg equals 1 g cm^{2}s^{-2}).

$$R = 8.31 \times 10^7 \text{ erg/mol K} = 8.31 \times 10^7 \text{ g cm}^2\text{s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$$
$$T = 273 + 37 = 310 \text{ K}; \; M = 32 \text{ g/mol}$$

Substituting these values in the equation

$$u_{rms} = \left[\frac{3 \times 8.31 \times 10^7 \text{ g cm}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1} \times 310 \text{ K}}{32.0 \text{ g mol}^{-1}}\right]^{1/2} = 4.92 \times 10^4 \text{ cm s}^{-1}$$

Example 6.13 The density of hydrogen at 0°C and 760 mm Hg pressure is 0.00009 g/cc. What is the root-mean-square speed of hydrogen molecules?

$$PV = \tfrac{1}{3} mN <u^2>$$
$$\text{Therefore,} \; <u^2> = 3PV/mN$$

*However, it is found that even at absolute zero all molecules possess a small residual energy known as a *zero point energy*. The existence of this energy is connected with the uncertainty principle (Chapter 3) and it is due to small oscillations of the atoms about their equilibrium positions in the crystal.

As m is the mass of a molecule and N, the number of molecules, mN is, therefore, the total mass; so $\rho = \text{mass/volume} = mN/V$ and $<u^2> = 3P/\rho$ or $u_{rms} = (<u^2>)^{1/2} = (3P/\rho)^{1/2}$. Now,

$$P = 760 \text{ mm} = 76 \text{ cm} = 76 \times 13.59 \times 981 \text{ dyne/cm}^2$$
$$\rho = 0.00009 \text{ g/cc}$$

Hence,

$$u_{rms} = \left[\frac{3 \times 76 \times 13.59 \times 981}{0.00009 \text{ g/cc}} \text{ dyne/cm}^2 \right]^{1/2}$$

$$= \left[\frac{3 \times 76 \times 13.59 \times 981 \times \text{g cm/s}^2 \text{ cm}^2}{0.00009 \text{ g/cc}} \right]^{1/2}$$

$$= 183.800 \times 10^3 \text{ cm/s} = 1.838 \text{ km/s}$$

6.11 HEAT CAPACITIES: TRANSLATIONAL, ROTATIONAL AND VIBRATIONAL DEGREES OF FREEDOM

So far we have shown how by using a simple molecular model it is possible to derive a theoretical equation that is consistent with the empirical gas laws; we also find that we can interpret the absolute temperature as a measure of the average molecular kinetic energy of translation. Let us pursue this and see if we can identify another macroscopic property, heat capacity, with the kinetic energy calculated by means of kinetic theory.

From the fundamental equation of the kinetic theory, the average translational energy for one mole of gas is

$$<\overline{KE}> = \tfrac{1}{2} mN_0 <u^2> = \tfrac{3}{2}RT$$

If all the thermal energy of a gas is in the form of translational energy we can write

$$\overline{E} = \tfrac{3}{2} RT$$

where the symbol $\overline{E}$ stands for the molar thermal energy. The *heat capacity* of any substance is defined as the quantity of heat required to raise the temperature by one degree and is equal to the increase in thermal energy of the system for this change of temperature. Hence, the heat capacity per mole, called the molar heat capacity ($\overline{C}_V$) at constant volume is

$$\overline{C}_V = d\overline{E}/dT = \tfrac{3}{2} R$$

Since R has a value of 1.987 cal/deg.mole this equation predicts the heat capacity of a gas to be approximately 3.0 cal/deg.mole and to be independent of temperature.

The prediction of the kinetic model is accurate for monatomic gases (Table 6.7), but the observed heat capacities of diatomic molecules are quite different. It is reasonable to assume that the discrepancy for diatomic and polyatomic molecules is connected with the increased complexity of the structure of these molecules and in particular, with the ways in which these molecules can absorb energy. Unlike in monatomic gases where all the energy is in the form of kinetic energy, in diatomic and polyatomic molecules energy is also associated with rotational and vibrational motions.

At this stage, we shall state the *law of equipartition of energy* according to which (i) each translational and rotational degree of freedom in a molecule contributes $\tfrac{1}{2}RT$ to the thermal energy of one mole of a gas, and (ii) each vibrational degree of freedom in a molecule contributes RT to the thermal energy of one mole of a gas.

The *degrees of freedom* in a molecule are given by the number of coordinates required to locate all the mass points (atoms) in a molecule. If a molecule contains only one atom (as in a monatomic gas), it has three degrees of freedom corresponding to translational motion in the three independent spatial directions X, Y, and Z. If a molecule contains N atoms, each atom contributes these three degrees of freedom, so the molecule has a total of $3N$ degrees of freedom. Since three coordinates (degrees of freedom) are required to represent the translational motion of the molecule, the remaining ($3N-3$) coordinates represent what are called the internal degrees of freedom. If the molecule is linear, it has two rotational degrees of freedom; for a non-linear molecule, there are three rotational degrees of freedom. The remaining degrees of freedom, that is $3N-5$ for linear and $3N-6$ for non-linear molecules are the vibrational de-

grees of freedom. Table 6.6 lists the degrees of freedom for several molecules. Fig. 6.22 gives a pictorial representation of various modes of motion for a typical polyatomic molecule.

(a) Translation

(b) Rotation

(c) Vibration

Xenon   Fluorine
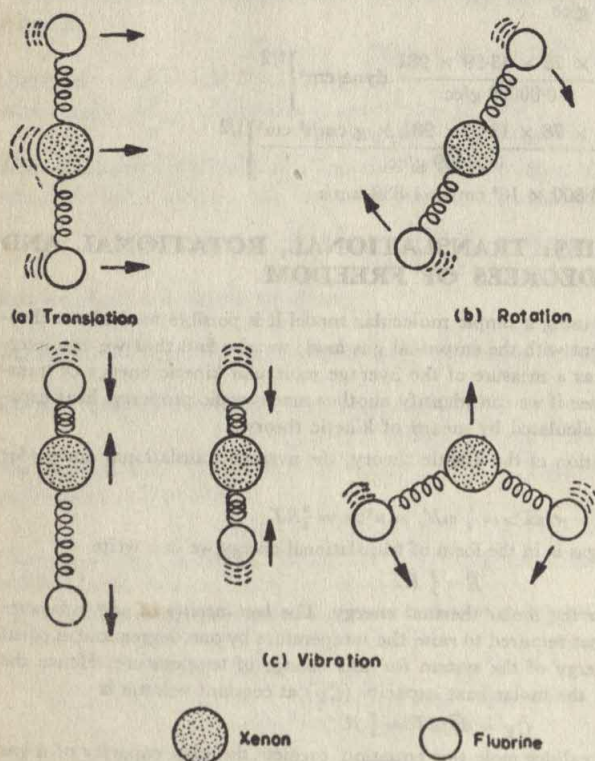
Fig. 6.22 Representation of various modes of motion of a linear triatomic molecule (XeF_2)

In a monatomic molecule, $\bar{E} = 3RT/2$ in agreement with the simple model. For a diatomic molecule, there are three translational, two rotational (because the molecule is linear) and

Table 6.6 Degrees of Freedom in Gaseous Molecules

Type	Molecule	trans	rot	vib	Total
Monatomic	He	3	0	0	3
Diatomic	N_2	3	2	1	6
Triatomic					
linear	CO_2	3	2	4	9
non-linear	H_2O	3	3	3	9

one vibrational degrees of freedom making a total of six. The thermal energy per mole would, therefore, be,

$$\bar{E} = (\tfrac{3}{2} RT)_{\text{trans}} + (\tfrac{2}{2} RT)_{\text{rot}} + (1 RT)_{\text{vib}}$$

and

$$\bar{C}_V = 3R/2 + R + R = 7R/2 = 7 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

Table 6.7 shows that the observed values of $\bar{C}_V$ for diatomic molecules deviate greatly from the predicted value. The fact that the value of 5 cal deg^{-1} mol^{-1} (which is close to $5R/2$) is most common for simple diatomic molecules suggests the possibility that heat capacity in these

molecules arises from translation and rotation and that vibrational motion does not contribute to the thermal energy at this temperature.

A proper explanation of the heat capacities of diatomic and polyatomic molecules is given by the quantum theory, according to which translational, rotational and vibrational energy changes can take place only in finite increments or quanta. At low temperatures, it is only translational energy which contributes to the heat capacity; as the temperature is raised, there

Table 6.7 Molar Heat Capacities, $\bar{C}_V$, of Some Gases in cal deg^{-1} mol^{-1} at 25°C

Gas	Formula	Mol. mass	$\bar{C}_V$	Gas	Formula	Mol. mass	$\bar{C}_V$
Monatomic				Oxygen	O_2	32	5·05
Argon	Ar	40	2·98	Nitric oxide	NO	30	5·11
Helium	He	44	2·98				
Mercury	Hg	201	2·98	Triatomic			
Diatomic				Carbon dioxide	CO_2	44	6·92
Hydrogen	H_2	2	4·91	Sulphur dioxide	SO_2	64	7·3
Nitrogen	N_2	28	4·95	Polyatomic			
Carbon				Ammonia	NH_3	17	6·57
monoxide	CO	28	4·97	Ethane	C_2H_6	30	10·65
Hydrogen chloride	HCl	36	5·01				

will be rotational contributions followed by vibrational contributions. For most diatomic molecules at room temperature, all the translational and rotational degrees of freedom are fully 'active' while the vibrational degree of freedom becomes 'active' only at higher temperatures. This is why the heat capacity of all diatomic gases approaches a value of 7 cal deg^{-1} mole^{-1} at high temperature (Fig. 6.23).
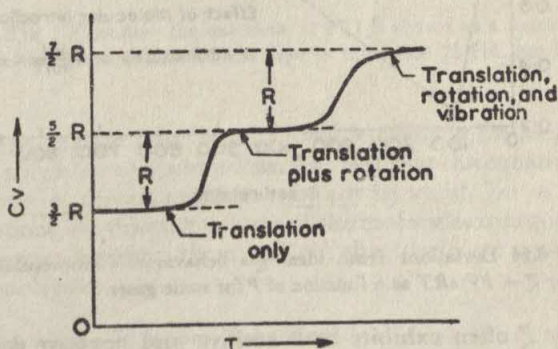
Fig. 6.23 Variation of heat capacity at constant volume of a diatomic gas due to excitation of rotational and vibrational levels

From the equipartition theorem, we can predict the high temperature heat capacity of monatomic solids. As the atoms in a solid can undergo only vibrational motion, each atom has three vibrational degrees of freedom. Thus, the thermal energy for a mole of solid is, $E=3\,RT$ and the molar heat capacity is $\bar{C}_V=3R\approx6$ cal deg^{-1} mol^{-1}. This equation agrees with the empirical results of Dulong and Petit according to which the heat capacity of one gram atom of a solid element is approximately 6.3 cal deg^{-1}.

6.12 DEVIATIONS OF GASES FROM IDEAL BEHAVIOUR

The PVT behaviour of gases has so far been presumed to follow the ideal gas equation, $PV=nRT$. This elegantly simple equation of state is at least approximately obeyed by almost all gases. Such behaviour is said to be ideal or perfect. When measurements are carried out at high pressures or low temperatures, no real gas is found to obey the ideal gas equation. A convenient way of showing the deviation of real gases from ideal behaviour is to write the ideal gas equation in the form, $PV=ZnRT$ where Z is unity. Or,

$$Z=PV/nRT=1 \quad \text{for an ideal gas}$$

The quantity $Z=PV/nRT$ is called the *compressibility factor*; $Z=1$ under all conditions for an ideal gas and the departure of a real gas from ideality is then measured by the deviation of the compressibility factor from unity. The extent of deviation from ideality depends upon the temperature and pressure.
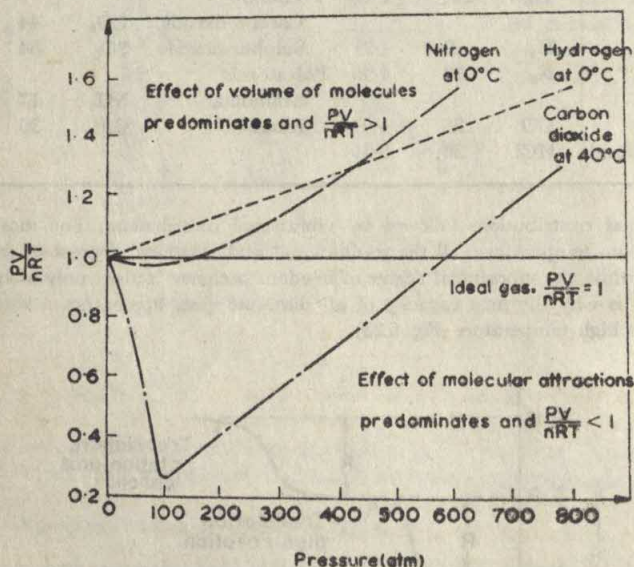
Fig. 6.24 Deviations from ideal gas behaviour. Compressibility factor $Z = PV/nRT$ as a function of P for some gases.

The quantity Z often exhibits both positive and negative deviations from unity. Fig. 6.24 shows some examples of the non-ideal behaviour of real gases. We see that even at 1 atm pressure there are small deviations from ideality for all gases at any temperature. The extent of deviation at any given temperature and pressure, of course, depends on the nature of the gas. Z approaches unity only in the vicinity of zero pressure which means that $PV=nRT$ is only a limiting law which applies exactly only at zero pressure. However, at finite but low pressures, it provides a useful approximation. The molar volume of an ideal gas (22·414 litres at STP) is not a measurable quantity but is obtained by plotting PV per mole of gases as a function of pressure and extrapolating the curves to $P = 0$ (Fig. 6.25). All extrapolated curves intersect the PV axis

at 22·414 since all gases behave ideally in the limit of zero pressure. In Table 6.8 are listed molar volumes at STP of some real gases.
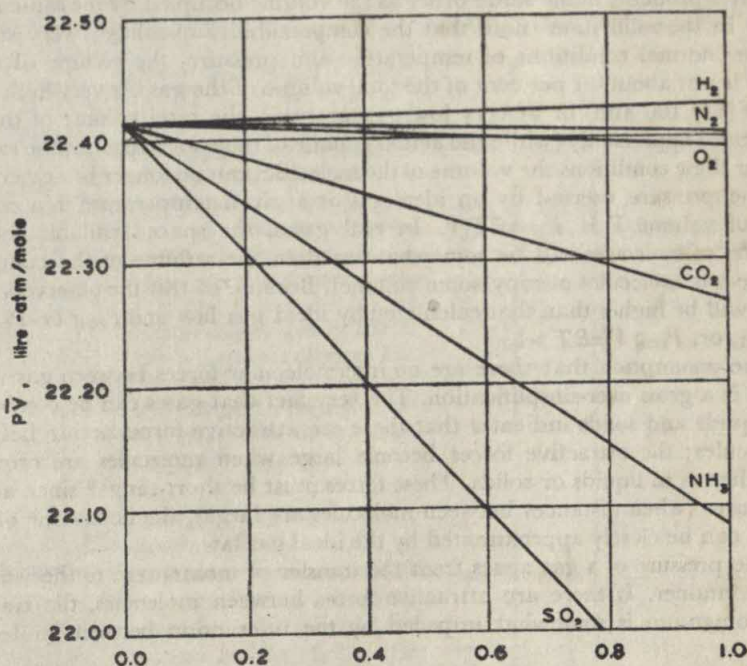
Fig. 6.25 The PV product for one mole at 0°C is shown as a function of pressure for several gases. These all converge to the value 22·414 litre atm/mol as $P \rightarrow 0$.

Why do gases deviate from ideality? While deriving the ideal gas equation, we had made a number of assumptions. The fact that this equation is not obeyed means that some of the assumptions may not be valid. Let us reexamine two of the assumptions (i) that the volume of the molecules is negligible compared to the empty space between them and (ii) that there are no attractive forces between the molecules.

Table 6.8 Molar volume, $\bar{V}$, of Some Gases at STP

Gas	Formula	Molar Volume, $\bar{V}$ (in litres)	Gas	Formula	Molar Volume $\bar{V}$ (in litres)
Ideal	—	22·4136	Oxygen	O_2	22·394
Hydrogen	H_2	22·428	Nitric oxide	NO	22·389
Helium	He	22·426	Carbon dioxide	CO_2	22·256
Nitrogen	N_2	22·404	Ammonia	NH_3	22·094

We know that the volume of a gas can be reduced by applying pressure or by cooling the gas until the gas condenses into a liquid or solid (with finite volume). This implies that molecules in the gas must also occupy some volume, which is probably of the same order as the volume occupied by the same molecules in the solid state (note that the compressibility of solids is very small). Under normal conditions of temperature and pressure, the volume of molecules is just about 0·1 per cent of the total volume of the gas. At very high pressures (say 100 atm) or at very low temperatures, the total volume of the gas decreases appreciably (while the actual volume of molecules remains the same); under these conditions the volume of the molecules can no longer be neglected.

The pressure exerted by an ideal gas at a given temperature in a container of volume V is, $P = nRT/V$. In real gases, the space available for the motion of molecules will be somewhat less than the volume of the container (since gas molecules occupy some volume). Because of this the observed pressure will be higher than that calculated by ideal gas law and P_{real} or $P_{obs} > P_{ideal}$, or, $P_{real} V/nRT > 1$.

The assumption that there are no intermolecular forces between gas molecules is a gross over-simplification. The very fact that gases can be condensed to liquids and solids indicates that there are attractive forces acting between molecules; the attractive forces become large when molecules are crowded together as in liquids or solids. These forces must be short-range* since at low pressures (when distances between molecules are large), the behaviour of real gases can be closely approximated by the ideal gas law.

The pressure of a gas arises from the transfer of momentum to the walls of the container. If there are attractive forces between molecules, the transfer of momentum is somewhat impeded by the interaction between molecules
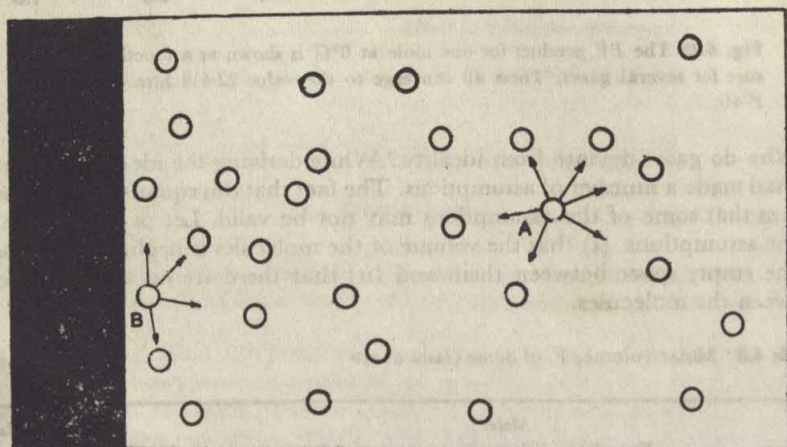
Fig. 6.26 Intermolecular interaction. A represents a typical molecule in the bulk of the gas and B a typical molecule in the boundary layer near a wall. Molecule A experiences, on the average, a resultant force of zero. Molecule B, on the other hand, experiences a net force tending to pull it toward the interior.

*That is, they become significant only when the distance between molecules is of the order of say 5 A. At large distances (10–15 A) they are negligible.

(Fig. 6.26). Consequently, the pressure will be reduced or $P_{real} < P_{ideal}$. Thus, presence of attractive forces between molecules tend to make $(P_{real}\ V/nRT)$ < 1 unlike the effect of actual volume of gases which causes $(P_{real}\ V/nRT > 1)$.

In Fig. 6.25, the regions where these two effects predominate are shown. For hydrogen at 0°C, the molecular attractive forces are weak and the size effect dominates its behaviour. For nitrogen at 0°C, the attractive forces are large enough to cause negative deviation up to about 150 atm, beyond which the size effect dominates. For CO_2, intermolecular attraction is large even at 40°C. The two effects compensate each other at 150 atm and 600 atm respectively in N_2 and CO_2 and $PV/nRT = 1$. At very low pressures gas molecules are widely separated and both these effects become negligible. Accordingly, as the pressure is decreased, the behaviour of gases approximate more and more closely that of the ideal gas (see Figs. 6.24 and 6.25). At high temperatures, molecules possess greater kinetic energy and their tendency to aggregate decreases and the behaviour of gases is close to the ideal gas behaviour. Thus, we see that under the normal conditions in the laboratory, deviations from ideality would be of the order of 1–2 per cent for most gases.

6.12.1 Intermolecular Forces and Joule–Thomson Effect

Intermolecular forces are both attractive and repulsive. The general way in which the force (F_r) between two molecules varies with distance is shown in Fig. 6.27; the variation of potential energy, $V(r)$, with distance, r, is also shown in this figure. (The relation between $F(r)$ and $V(r)$ is the following; the work done in producing a small increase Δr in r, $F(r)\Delta r$ is equal to the decrease in the potential energy.) The potential energy is usually taken to be zero when the molecules are separated by an infinite distance. As r decreases from infinity, the attractive forces increase and the energy V decreases. After reaching a minimum value, the potential energy rises abruptly as the molecules are brought still closer and the forces between them become repulsive. The distance σ (Fig. 6.27) gives the minimum distance of approach of two molecules and in a sense, it is a measure of the diameter of the molecules.* When the distance is between r_0 and r, the forces are attractive and it is these forces that are responsible for the condensation of gases.
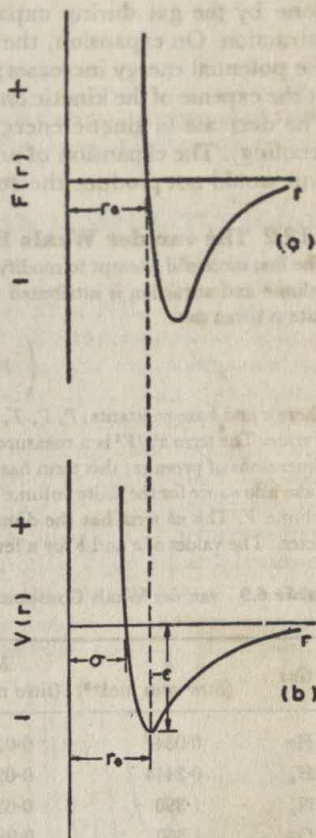
Fig. 6.27 The variation of (a) the force and (b) the mutual potential energy of a pair of molecules with distance.

The parameter ϵ is equal to the minimum value of the potential energy and is often referred to as the 'depth' of the potential energy 'well'. The distance parameter σ is equal to the minimum distance of approach of two molecules at which the potential energy is zero. The values of ϵ and σ depend upon the nature of the interacting molecules.

*The size of a molecule is an ill-defined quantity but nevertheless is quite a useful concept.

The most convincing experimental evidence for the existence of attractive intermolecular forces was obtained by J.P. Joule and W. Thomson (1852). They showed that when a compressed gas is allowed to expand in a thermally insulated apparatus, the temperature decreases.* This phenomenon is called the *Joule-Thomson effect*. The fall in temperature is attributed to the work done by the gas during expansion to overcome the intermolecular forces of attraction. On expansion, the distance between molecules increases and hence the potential energy increases; this increase in potential energy must take place at the expense of the kinetic energy if the energy of the system is to be conserved. The decrease in kinetic energy is then observed as a decrease in temperature (cooling). The expansion of an ideal gas in which there are no forces of attraction would not produce the cooling effect.

6.12.2 The van der Waals Equation

The first successful attempt to modify the ideal gas equation in order to correct for the molecular volume and attraction is attributed to van der Waals (1873). The van der Waals equation of state is given as

$$\left(P + \frac{n^2a}{V^2}\right)(V-nb) = nRT$$

where a and b are constants; P, V, T, n and R have the same meaning as in the ideal gas equation of state. The term n^2a/V^2 is a measure of the attractive forces between gas molecules and has the dimensions of pressure; this term has to be added to the measured P to get the ideal pressure. To make allowance for the finite volume of gas molecules, we subtract the term nb from the measured volume V. This nb term has the dimensions of volume and is a function of the molecular diameter. The values of a and b for a few gases are given in Table 6.9.

Table 6.9   van der Waals Constants

Gas	a (litre^2 atm mol^{-2})	b (litre mol^{-1})	Gas	a (litre^2 atm mol^{-2})	b (litre mol^{-1})
He	0·0341	0·0237	NH_3	4·170	0·03707
H_2	0·2444	0·02661	H_2O	5·464	0·03049
N_2	1·390	0·03913	H_2S	4·431	0·04287
O_2	1·360	0·03183	Xe	4·194	0·05105
CO_2	3·592	0·04267			

Example 6.14   Calculate the pressure exerted by 5·0 moles of carbon dioxide in a 1 litre flask at 47°C, using (a) the van der Waals equations and (b) the ideal gas law. Compare these results with the experimentally observed pressure of 82 atm.

(a) The van der Waals equation is,

$$\left(P + \frac{n^2a}{V^2}\right)(V-nb) = nRT$$

$P = ?$

$n = 5\cdot0$ mol

$V = 1$ litre

$T = 47 + 273 = 320$ K

$R = 0\cdot0821$ litre atm mol^{-1} K^{-1}

*This is only true in the Joule-Thomson experiment if a gas is below the inversion temperature.

From Table 6.9 $a=3.592$ litre^2 atm mol^{-1} and $b=0.0427$ litre mol^{-1}. Substituting these values

$$\left(P + \frac{25 \times 3.592}{1}\right)(1.0 - 5.0 \times 0.0427) = 5.0 \times 0.0821 \times 320$$

$$(P + 25 \times 3.592)(0.7865) = 5.0 \times 0.0821 \times 320$$

$$P = \frac{5.0 \times 0.0821 \times 320}{0.7865} - 25 \times 3.592 = 77.2 \text{ atm}$$

(b) For an ideal gas, $PV = nRT$

$$P \times 1.0 = 5.0 \times 0.0821 \times 320$$

$$P = 5.0 \times 0.0821 \times 320 = 131.3 \text{ atm}$$

The pressure calculated from the van der Waals equation is closer to the experimental value (82 atm). This is to be expected because the total pressure of the gas is high enough to cause significant deviations from the ideal behaviour.

6.13 LIQUEFACTION OF GASES: CRITICAL TEMPERATURE AND PRESSURE

By the middle of the 19th century a number of gases like NH_3, SO_2, CO_2, H_2S and N_2O were liquefied by the combined effect of compression and cooling. Liquefaction is easy to understand from the microscopic viewpoint since the kinetic energy of the molecules decreases on cooling. As a result of this, some of the molecules get closer to one another till they change into the liquid state. High pressure also favours liquefaction because molecules are brought sufficiently close together to permit the attractive forces to be large enough to cause condensation. It is possible to liquefy most of the gases at atmospheric pressure, but it is quite impossible to liquefy many gases at ordinary temperatures. Gases like hydrogen, oxygen, and nitrogen cannot be liquefied at laboratory temperatures even under pressure of several thousand atmospheres.

The essential condition for liquefaction was discovered by Andrews (1863). He demonstrated that there exists for each gas a certain temperature, called the *critical temperature*, above which it cannot be liquefied, no matter how great the pressure. Andrews studied the pressure–volume realtion of CO_2 at different temperatures and his results are shown in Fig. 6.28. The isotherm T_7 represents the data obtained at a relatively high temperature. Its form is very close to that of a rectangular hyperbola and shows that at this temperature CO_2 follows Boyle's law rather closely.

Now consider the isotherm T_1 which is below the critical point. As the vapour is compressed, the P-V curve follows AB which is roughly in accordance with Boyle's law. When the point B is reached liquid CO_2 is formed and this can be observed by the appearance of a meniscus between vapour phase and liquid phase. As the volume decreases further, more of the gas is transferred to the liquid phase while the pressure remains constant (note the flat portion of the curve). Finally at C all of the CO_2 is in the liquid phase and the curve CD is the isotherm of liquid CO_2. Since the liquids are relatively in-

Fig. 6.28 Andrews' isotherms for CO_2

compressible, the compression of the liquid from C to D results in little volume change and hence the curve CD is very steep.

The flat part of the isotherm reveals an important fact that as long as both liquid and gas phases are present, the pressure of the gas in contact with the liquid must be the same, quite independent of whether a small or a large fraction of the volume is occupied by liquid. This equilibrium pressure is known as the vapour pressure of the liquid at that particular temperature. As isotherms are taken at successively higher temperature we find that the flat part, i.e. the volume range in which the phases coexist, becomes shorter and shorter until for a particular isotherm (T_5) its length is reduced to zero at the point ' P.' This is the critical point and the isotherm on which it lies is the critical isotherm. This temperature is known as the *critical temperature*.

The pressure at the critical point is known as the *critical pressure* (P), and the corresponding volume per mole is called the *critical molar volume*. It is to be noted that at the critical temperature, liquid and vapour of a substance become so similar that they can no longer be distinguished as individuals. The indices of refraction, densities and molar volumes of the two phases become identical in the critical state. Andrews observed that ' If any one asked whether it (the substance in this state) is now in the gaseous or in the liquid state, the question does not, I believe, admit of a positive reply '.

The critical temperature of carbon dioxide was found by Andrews to be 31·2°C and it is clear from his results that above this temperature, even the highest pressure can never yield a state with a meniscus. The observations of Andrews regarding carbon dioxide, are generally valid for all other substances. The actual temperature, pressure and volume vary from one substance to another, but the nature of isotherms at different temperatures is much the same.

The critical constants for a number of substances are given in Table 6.10. Those gases whose critical tempera-

Fig. 6.29 Liquefaction of air. The cooling produced by the Joule-Thomson expansion is used to lower the temperature of gases to the point where liquefaction takes place. Compressed air below its Joule-Thomson inversion temperature is allowed to expand through a nozzle. Upon expansion, the air is cooled because it uses up kinetic energy to push back the atmosphere and to overcome the intermolecular forces. The cooler expanded air passes over the compressed coil and cools the incoming compressed air. The cooler compressed air, the cooler the expanded air becomes. Finally the incoming air is sufficiently cold so that part of it condenses to liquid which is drawn off at the bottom of the expansion chamber. Liquid air boils at about − 190°C and is roughly 750 times as dense as atmosphere air.

tures lie below room temperature, such as nitrogen and oxygen, cannot be liquefied by pressure alone without strong cooling and that is why early attempts to liquefy them failed. The work of Andrews clearly showed the need to cool such gases below the critical temperature to achieve liquefaction. A schematic diagram of an apparatus used to liquefy air is shown in Fig. 6.29.

Table 6.10 Critical Temperatures, Pressures and Volumes

Gas	Critical temperature (K)	Critical pressure (atm)	Critical volume (cc/mol)	Gas	Critical temperature (K)	Critical pressure (atm)	Critical volume (cc/mol)
He	5·23	2·26	57·6	CO_2	304·2	73·0	95·7
H_2	33·3	12·8	65·0	NH_3	405·6	112·0	72·4
N_2	126·1	33·5	90·0	H_2O	647·2	218·5	56·0
O_2	154·4	49·7	74·4				

SUGGESTED READING

M. Born, *The Restless Universe*, Dover Publications Inc., New York, Chapter I.

R. P. Feynman, R. E. Leighton and M. Sands, *The Feynman Lectures on Physics*, Vol. I Addison-Wesley Publishing Co., Reading, Mass., 1965, Chapters 1 and 39.

J. H. Hildebrand, *An Introduction to Molecular Kinetic Theory*, Reinhold Publishing Co., New York, 1963.

PROBLEMS

6.1 What is the difference between pressure and force? Show that the diameter of the tube used to make a barometer does not effect the height of the mercury column. How do you measure the pressure of a gas?

6.2 Explain the following observations:
   (a) Aerated water bottles are kept under water during summer.
   (b) Liquid ammonia bottle is cooled before opening the seal.
   (c) The tyre of an automobile is inflated to slightly lesser pressure in summer than in winter.
   (d) The size of a weather balloon becomes larger and larger as it ascends up into higher altitudes.

6.3 Absolute temperature scales can be set up on bases other than the one described in this chapter. For example, an absolute scale can be defined which is based on the Fahrenheit rather than the centigrade temperature. Find the relationship between the absolute temperature and the temperature on Fahrenheit scale.

6.4 Which properties of a gas determine (a) the average speed of its molecules; (b) the average energy of its molecules; (c) the pressure it exerts; and (d) the force of an average molecule-wall collision?

6.5 Suggest explanations for the facts that gases (a) do not settle at the bottom of a container; (b) diffuse through all the space available to them; and (c) expand with increase in temperature.

6.6 *The molar volume of a gas is 22·4 litres.* Comment and write a more accurate statement about molar volume.

6.7 The average velocity of the molecules in a gas must be zero if the gas as a whole and the container are not in a translational motion. Explain how it can be that the average speed is not zero.

6.8 Justify the fact that the pressure of a gas depends upon the square of, the speed of its particles by explaining the dependence of pressure on the collision frequency and the momentum transfer of the particles.

6.9 Suppose there is a tiny sticky area on the wall of a container of gas. Molecules hitting this area stick there permanently. Is the pressure greater or less than on the ordinary areas of the walls?

6.10 Can a van der Waals gas with $a=0$ be liquefied? Explain.

6.11 In Table 6.8 why are some of the values of molar volume greater than the ideal value and why others are less? Do you see any correlation with the properties of the molecules?

6.12 The first evidence that noble gases are monatomic elements came from the interpretation of their measured heat capacities. Explain how such data can lead to the conclusion that a gas is monatomic or diatomic.

6.13 Suggest why there is no hydrogen (H_2) in our atmosphere. Why does the moon have no atmosphere?

6.14 Explain whether a gas approaches ideal behaviour or deviates from ideal behaviour if it is
(*a*) compressed to a smaller volume at constant temperature,
(*b*) temperature is raised keeping the volume constant,
(*c*) more gas is introduced into the same volume and at the same temperature.

6.15 At room temperature the C_v value of carbon tetrachloride is much in excess of 6 cal/mole °C. How can one account for such a behaviour?

6.16 The best vacuum pump can generate a vacuum of about 10^{-9} mm. Calculate the number of molecules which still remain in 1 cc of the apparatus at 27°C.

6.17 How many moles, molecules and atoms of phosphorus are contained in 92·93 g of phosphorus, if the formula of its molecule is P_4.

6.18 It takes 0·4 g of nitrogen to fill a bulb at 25°C and 1 atm while it takes 0·8 g of an unknown gas A to fill the same bulb under the same conditions of temperature and pressure. What is the molecular mass of the unknown gas?

6.19 A gas is enclosed in a room. The temperature pressure, density and number of moles respectively are $t°$ C, p atm, ρ g/litre and n moles.
(*a*) What will be the pressure, temperature density and number of moles in each compartment if the room is partitioned into four equal compartments?
(*b*) What will be the values of pressure, temperature, density and number of moles in each compartment if the wall between any two compartments, say, 1 and 2, is removed?
(*c*) What will be the values of pressure, temperature, density and number of moles if an equal volume of the gas at pressure p and temperature t is let in the same room?

6.20 Two flasks, A and B of equal volume are connected by a narrow tube whose volume may be considered negligible as compared with the volume of the flasks. The flasks contain 0·7 mol of hydrogen gas at 0·5 atm pressure and 27°C. The flask A is then immersed in a bath kept at 127°C while the flask B is still maintained at 27°C. Calculate the final pressure and the moles in each flask.

6.21 An underwater bubble with a diameter of 1 cm at the bottom of a tank where the temperature is 5°C and the pressure is 3 atm rises to the surface, where the temperature is 25°C and the pressure is 1 atm. What will be the diameter of the bubble when it reaches the surface? Ignore the presence of water vapour in the bubble.

6.22 The *J*-shaped tube shown in the figure is filled initially with air at 1.00 atm and 25°C. Liquid mercury is then poured into the open end. Calculate (*a*) the height of the mercury column in the long arm when mercury is just starting to spill over the top of the short arm and (*b*) the pressure of the trapped air at this point.

100 cm

40 cm
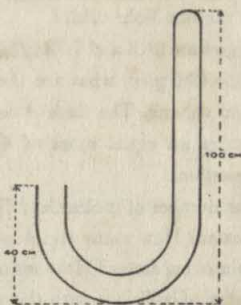
6.23 A 1-litre bulb weighs 38·7340 g when empty and 40·0269 g when filled with dry air at STP. Assuming that air is an ideal gas and that it consists entirely of oxygen and nitrogen determine (a) the average molecular mass and (b) the composition of the air. The average molecular mass is defined as total mass/total moles.

6.24 The composition of dry air by volume percentage is N_2 78·1%; O_2 21·0%; and Ar 0·9%. Calculate the density in g/litre of air saturated with water vapour at 25°C. The vapour pressure of water at this temperature is 23·7 mm.

6.25 If chlorine gas is 70 mole per cent dissociated at 2000 K and 1 atm to form atomic chlorine, what is the density of the gas? (Atomic mass of chlorine=35·5)

6.26 A given sample of dry methane occupies a volume of 368 ml at 21°C and 752 mm pressure. Suppose this sample is now bubbled through water at 21°C until it gets saturated with water vapour. If the pressure of wet gas is 752 mm, what volume will the wet gas have to occupy? The vapour pressure of water at 21°C is 18·7 mm.

6.27 1·47 litre of a gas is collected over water at 30°C and a barometric pressure of 744 mm. If the gas has a weight of 1·98 g and the vapour pressure of water at 30°C is 32 mm what is the molecular mass of the gas?

6.28 In a gaseous mixture at 20°C, the partial pressures of the components are as follows: H_2=200 mm, CO_2=150 mm, CH_4=320 mm, C_2H_4=105 mm. What is the volume percentage of each component in the mixture?

6.29 Uranium isotopes have been separated by taking advantage of the different rates of diffusion of the two isotopes of UF_6. One form contains uranium of atomic mass 238 and the other of atomic mass 235. What are the relative rates of diffusion of these two molecules under ideal conditions?

6.30 16 cc of hydrogen was found to diffuse in 30 s. What volume of sulphur dioxide could diffuse in the same time under the same conditions?

6.31 A mixture consisting of 80 mole per cent hydrogen and 20 mole per cent deuterium at 25°C and at a total pressure of 1 atm is permitted to effuse through a small orifice of area 0·20 mm². Calculate the composition of the initial gas that passes through.

6.32 Calculate the pressure exerted by 10^{23} gas particles, each of mass 10^{-22} g in a container of volume 1 litre. The root-mean-square speed of the particles is 10^5 cm s^{-1}. What is the total kinetic energy of these particles? What must be the temperature?

6.33 The tip of a lady's hair-pin sticking out of her hair-do is exposed to atmospheric pressure at 27°C. Calculate the number of gas molecules hitting the tip per second if the tip has a diameter of 10^{-4} metre. Assume that air is an ideal gas mixture consisting of 80 mole per cent nitrogen and 20 mole per cent oxygen at a pressure of 1 atm.

6.34 Calculate the temperature at which the root-mean-square speed of sulphur dioxide molecule is the same as that of oxygen at 27°C.

6.35 Compute the temperature at which the root-mean-square speed for hydrogen is equal to the escape velocity from the surface of earth.

6.36 At what temperature is the average translational energy of a molecule is equal to the kinetic energy of the electron in the first Bohr orbit?

6.37 If the densities of helium and argon are $0 \cdot 18$ and $1 \cdot 78$ g/litre respectively at a barometric height of $76 \cdot 0$ cm (density of $Hg = 13 \cdot 6$ g/cc) what are their respective speeds?

6.38 Two flasks A and B have equal volume. The flask A contains H_2 and is maintained at 300 K while the flask B contains an equal mass of CH_4 gas and is maintained at 600 K. Answer the following questions:

(*a*) Which flask contains greater number of molecules? How many times more?

(*b*) In which is the pressure greater? How many times as great?

(*c*) In which are the molecules moving faster? How many times as fast?

(*d*) In which flask are the number of collisions with the wall greater? How many times as great?

(*e*) In which is the kinetic energy per mole greater? How many times as great?

(*f*) In which flask is the total kinetic energy greater? How many times as great?

(*g*) To which flask would you give more heat to raise its temperature by one degree, assuming (though this is not true) that all degrees of freedom contribute fully to the thermal energy of the molecules. Explain.

6.39 $11 \cdot 2$ litre of an unknown gas at STP requires 25 cal to raise its temperature by $10°C$ at constant volume. Calculate C_v for the gas. What can you conclude about its structure?

6.40 The specific heat for a gas at constant volume is $0 \cdot 075$ cal g^{-1} deg^{-1} and at constant .pressure is $0 \cdot 125$ cal g^{-1} deg^{-1}. Calculate the molecular mass of the gas.

6.41 Compute the average translational and average rotational energy of a non-linear triatomic molecule such as SO_2 at $25°C$. At $25°C$ only one of the vibrational modes of SO_2 contributes fully to the average energy of the molecule. How much of this contribution adds to the average energy? Calculate C_v for SO_2 at this temperature.
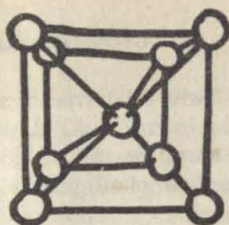
The Solid State

The infinite variety in the properties of the solid materials we find in the world is really the expression of the infinite variety of the ways in which the atoms and molecules can be tied together, and of the strength of those ties. We shall never thoroughly understand the materials that we put to use every day, nor grasp their design, until we have found out at least the arrangement of the atoms and molecules in the solid, and are able to test the strength and other characteristics of the forces that hold them together.

WILLIAM BRAGG

In the gaseous state, molecules move randomly without exerting appreciable forces on one another. In the solid state, on the other hand, there is regular order in the arrangement of atoms or molecules constituting the solid and these are held together by fairly strong forces. The important macroscopic properties of solids are rigidity, characteristic geometry and extremely low compressibility. In this chapter, we shall address ourselves to three questions. What are the main structural features of solids? What are the properties of solids? How can we explain these properties on the basis of the microscopic approach? A proper understanding of the nature and properties of solids provides the basis for developing new tailor-made materials with desired properties which can be used in many devices. Much of the recent progress in science and technology is undoubtedly due to the advances made in the chemistry and physics of solid materials.

7.1 MACROSCOPIC PROPERTIES OF SOLIDS

Many of the macroscopic properties of solids are familiar to us through common experience. Some of these important properties are: (*i*) Solids are rigid and have definite shape. (*ii*) Solids maintain their volume independent of the size or shape of the container in which they are kept. (*iii*) Solids are nearly incompressible. (*iv*) Solids diffuse very slowly compared to liquids or gases. (*v*) Solids can form crystals. All these properties suggest that atoms or molecules constituting a solid occupy fixed positions in contact with each other. The term crystal comes from the Greek word *krystallos* which means clear ice. This term was first applied

239

to the beautiful transparent quartz stones found in the Swiss Alps, due to the belief that these stones were formed from water by the intense cold. Later, however, the name was used for solids bounded by many flat shiny faces symmetrically arranged. In Fig. 7.1 are shown magnified photographs of ordinary snow-flakes which are indeed crystals of ice.
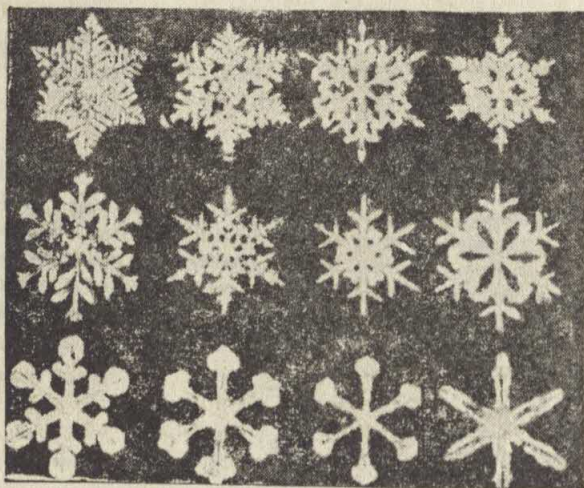
Fig. 7.1 Ordinary snowflakes (magnified photograph) show regularity not unlike that exhibited by natural crystals of other compounds. Snowflakes are indeed crystals of ice.

Fig. 7.2 Crystal forms of some common materials

Crystals of a given substance are bounded by plane surfaces called *faces* and these faces intersect at angles characteristic of the crystalline substance. In Fig. 7.2 are shown shapes of crystals of three common substances, alum, sodium chloride and quartz. Whenever we try to break or cut a crystal, it splits or cleaves along preferred directions and the characteristic shapes (faces and angles) are found in the resulting pieces as well. Many substances crystallise in more than one form and this phenomenon is referred to as *polymorphism* or *allotropy*; in Greek. *polymorph* means many forms.

The most important feature of crystals is the highly ordered periodic arrangement of the constituent atoms, ions or molecules. All solids need not be crystalline. There are many solid materials which are amorphous and do not exhibit the ordered arrangement of the constituent units. Glasses, for example, exhibit many of the properties of solids such as rigidity and slow diffusion, but there is little order in the arrangement of units.* Electrical, mechanical and other properties of crystals generally depend on the direction along which they are

*Glassy state can be considered to be another state of matter, since a glass is a super cooled liquid.

measured. Such a behaviour is called *anisotropy*. Amorphous materials are generally isotropic, i.e. the properties do not depend on the direction of measurement. Anisotropy is a clear indication of the presence of ordered lattices in crystals. In gases and liquids, where molecules or atoms move randomly, all directions are equivalent. Another important property characteristic of a crystalline solid is the sharp melting point at which the solid turns into liquid. Amorphous solids do not melt sharply, but show gradual softening until they start to flow.

Powders or finely ground samples of solids often appear as though they are amorphous. However, if we examine even a tiny particle under a microscope, characteristic features of crystals (like shape and angles) may become visible if the material is crystalline. It is important to recognise the difference between polycrystalline and amorphous solids. Polycrystalline solids possess the ordered atomic lattice, but the individual crystalline particles may be too small to be seen except under a good microscope. In nature, we find large crystals of many minerals. We can also grow good crystals of substances in the laboratory. While the size of a crystal depends on the conditions of growth, the internal atomic arrangement remains invariant with size. Further, crystals of a substance may exhibit different shapes due to external conditions of growth, but the angles between faces are always the same. This constancy of interfacial angles is an important universal property of crystals; this property is unique for a particular crystalline compound and provides a means of identifying the class a crystal belongs to.

7.2 TYPES OF SOLIDS

The highly ordered arrangement of the constituent units (atoms or molecules) in crystalline solids is responsible for their characteristic properties. Based on the nature of forces that bind these units, we can broadly divide solids into four types: covalent solids, ionic solids, molecular solids and metallic solids. This classification, although arbitrary, provides a basis to understand the similarities and differences in the various properties of solids. The essential features of these four types of solids are summarised in Table 7.1 and a more detailed discussion is given in the following sections.

7.2.1 Covalent Solids

Atoms comprising a covalent molecule like methane or hydrogen are held together by covalent or nearly covalent bonds (Chapter 4). In a covalent solid, similarly, atoms are connected to one another by covalent linkages forming a giant network. The units in these networks can either be atoms of the same element or atoms of different elements with similar electronegativities. Carbon, silicon and silicon carbide (SiC) are examples of covalent solids (see Chapter 16, section 5 for more details). In diamond (Fig. 7.3) each carbon atom is linked to four other carbon atoms through the four tetrahedrally oriented covalent bonds (carbon having sp^3 hybridisation), thus forming a three-dimen-
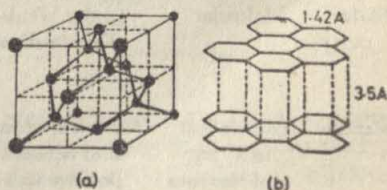
Fig. 7.3 Structures of (*a*) diamond and (*b*) graphite

sional network of carbon atoms. Silicon also has four valencies directed to the vertices of a tetrahedron. SiC has the same geometrical arrangement as diamond, the only difference being that each silicon atom is surrounded by four carbon atoms and vice versa. In graphite, the other allotropic form of carbon, where carbon has sp^2 hybridisation, infinite sheets of atoms are packed in a layer structure (Fig. 7.3) and the layers are held together by weak attractive forces (of the van der Waals type discussed in section 7.2.3). Boron nitride, BN, normally has the layer structure of graphite, but under high pressure and temperature, the diamond form can be prepared. Since covalent bonds are strong and directional, this type of solids are fairly hard and resist deformation.

7.2.2 Ionic Solids

Substances which form ion pair molecules in the gaseous phase (see section 4.7) generally condense at lower temperature to form ionic solids. The structural units in these solids are positive and negative ions. However, a particular negative ion cannot be associated with a particular positive ion (as in an ionic molecule) because in solids, each ion is surrounded by a definite number of ions of opposite charge. This number is controlled by the formula of the compound as well as by the relative sizes of the two ions. In sodium chloride crystals, each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions (see section 7.3.3). Electrostatic attraction, responsible for the stability of ionic molecules, also accounts for the stability of ionic solids.

It would be of interest to enquire why ionic solids like sodium chloride have the characteristic formula NaCl, or magnesium chloride, $MgCl_2$, but not the formulae $NaCl_2$ and MgCl. To understand why a compound with the formula

Table 7.1 Different Types of Solids and Their Properties

Type	Units present in the solid	Major binding force	Properties	Examples	Approximate energy required to separate units (kcal mol^{-1})
Covalent	Atoms	Shared electrons	Hard	C (diamond)	170
			High-melting	Si	105
			Non-conducting		
Ionic	Positive and negative ions	Coulombic or electrostatic attraction	Brittle	LiF	247
			Fairly high	NaF	216
			melting	NaCl	184
			Insulating	AgCl	216
Molecular	Molecules	van der Waals Dipole–dipole	Soft	Ar	1·6
			Low-melting	CO_2	6·0
			Volatile	CH_4	2·0
			Insulating	Cl_2	4·9
Metallic	Positive ions in a 'sea' of electrons (electron gas)[1]	Electrical attraction between positive ions and delocalised electrons	Low to high melting Highly conducting	Li Al Fe W	38 77 99 200

[1]This is only a crude description of a metal.

NaCl is stable whereas one with the formula $NaCl_2$ is not, we shall compute the net energy of the solid compound relative to the component ions in the gaseous state. The reaction of solid sodium metal with gaseous chlorine to give crystalline sodium chloride can be written as

$$Na(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$$
$$\text{or } Na(s) + Cl_2(g) \longrightarrow NaCl_2(s)$$
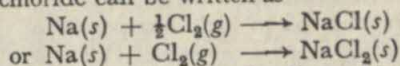
depending upon whether the formula of sodium chloride is NaCl or $NaCl_2$.

The energetics of these reactions can be worked out by breaking down the reactions into several steps such that the energy change, ΔE, in each step can be either calculated or measured. For NaCl, we obtain the following results:

Reaction	Process involved	Energy change in the process, ΔE (kcal mol^{-1})
1. $Na(s) \longrightarrow Na(g)$	Sublimation	$25 \cdot 4 = \Delta E_{sub}$
2. $Na(g) \longrightarrow Na^+(g) + e$	Ionisation	$118 \cdot 5 = IE$
3. $\tfrac{1}{2}Cl_2(g) \longrightarrow Cl(g)$	Dissociation	$27 \cdot 3 = \tfrac{1}{2}(D)$
4. $Cl(g) + e \longrightarrow Cl^-(g)$	Electron affinity	$-83 \cdot 4 = EA$
5. $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$	Total coulombic energy	$-206 \cdot 0 = U$

Adding, we get the net reaction,* Net energy change $-118 \cdot 2$
$= Na(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$ (formation energy)

The energy requirement of the first step is given by the measured heat of sublimation, of the second step by the ionisation energy of sodium atom, of the third step by the dissociation energy of chlorine molecule in the gaseous state and of the fourth step by the electron affinity of the chlorine atom. The last step represents the net coulombic attraction energy† among all the ions in solid NaCl and is obtained by calculating the attractive and repulsive energies between ions in the specific ordered arrangememt of ions (geometry) in the crystal. The result shows that crystalline NaCl is more stable than the gaseous sodium and chlorine by $118 \cdot 2$ kcal mol^{-1}.

Similar calculation can be performed for $NaCl_2$.

Reaction	$\Delta(E)$ (kcal mol^{-1})
1. $Na(s) \longrightarrow Na(g)$	$25 \cdot 4$
2. $Na(g) \longrightarrow Na^{2+}(g) + 2e$	$1208 \cdot 5$
3. $Cl_2(g) \longrightarrow 2\,Cl(g)$	$54 \cdot 6$
4. $2\,Cl(g) + 2e \longrightarrow 2\,Cl^-(g)$	$-166 \cdot 8$
5. $Na^{2+}(g) + 2\,Cl^-(g) \longrightarrow NaCl_2(s)$	$-620 \cdot 0$

Net reaction $= Na(s) + Cl_2(g) \longrightarrow NaCl_2(s)$ $+504 \cdot 0$

The second step here represents the energy to remove two electrons from sodium atom (the sum of the first and second ionisation energies of sodium). Similarly, the fourth step involves the sum of first and second electron affinities of chlorine

*The basis for adding and subtracting energy changes of reactions is discussed later in Chapter 9 (section 6).

†This energy, called the *lattice energy*, is discussed in detail later in this section.

atom. The energy of the last step is only approximate since $NaCl_2$ does not exist and it is not possible to know its lattice geomerty. However, the estimated value for this step is reasonable enough to indicate to us clearly that $NaCl_2$ is unstable with respect to sodium and chlorine vapour.

To summarise, the formula of an ionic compound of the formula MX is determined by the ionisation energy (or energies) of the electropositive atom M, by the electron affinity of the electronegative atom X and by the electrostatic attraction of the oppositely charged ions located at particular distances in the specific geometric arrangement of the ions in the crystal. The formation of a multiply charged cation is unfavourable from considerations of ionisation energy, but it is favourable from considerations of electrostatic attraction. The most stable arrangement is one which optimises these two opposing tendencies.

Lattice energy: In the discussion of the ion-pair molecule Na^+—Cl^- in section 4.7, we showed that the coulomb attraction between the oppositely charged Na^+ and Cl^- ions is responsible for the stability of the molecule. However, in crystalline state, the alternate presence of oppositely charged ions extends infinitely in three dimensions. We would expect such an ordered arrangement to be associated with much larger coulombic attractive energy. It is easy to visualise this if we first consider one row of ions as follows:

Na^+	Cl^-	Na^+	Cl^-	Na^+	Cl^-	Na^+	Cl^-	Na^+
$4r$	$3r$	$2r$	r	0	r	$2r$	$3r$	$4r$
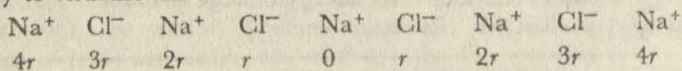
We can calculate the coulombic energy experienced by one Na^+ ion (shown by zero, 0, in the row of ions). The attractive energy due to a neighbouring Cl^- ion at distance r (internuclear distance in the solid) is $-e^2/r$; therefore, due to the two Cl^- neighbours, the attractive energy will be $-2e^2/r$. The interaction with the two nearest Na^+ ions at distance $2r$ (next to the Cl^- neighbours) would be repulsive and the contribution to the potential energy from this interaction would be $+2e^2/2r$. The interaction energy with Cl^- ions at $3r$ would be $-2e^2/3r$. We can write the interaction energy in a row of ions in the form of an infinite series of terms representing the interaction energies with Cl^- and Na^+ at various distances:

$$U_{row} = -\frac{2e^2}{r} + \frac{2e^2}{2r} - \frac{2e^2}{3r} + \frac{2e^2}{4r} + \dots$$

$$= -\frac{2e^2}{r}(1 - \tfrac{1}{2} + \tfrac{1}{3} - \tfrac{1}{4} + \tfrac{1}{5} - \tfrac{1}{6} + \dots)$$

$$= -\frac{2e^2}{r}\left[(1 - \tfrac{1}{2}) + (\tfrac{1}{3} - \tfrac{1}{4}) + (\tfrac{1}{5} - \tfrac{1}{6}) + \dots\right]$$

The first two terms in the series give an attractive energy of $-e^2/r$ corresponding to that of an ion-pair molecule. We see that every term in brackets gives a positive number and the total coulombic energy U_{row}, becomes more and more negative (or attractive) as we increase the number of terms in the series. This clearly shows how the potential energy of an ion in a one-dimensional row of ions is much lower than in a simple ion pair.

If we were to extend the calculation of the interaction energy to a three-dimensional array of ions as present in crystals, the potential energy would be still lower and the coulombic attractive energy in such a system can be repre-

sented in the form $-\alpha e^2/r$, where α is a constant depending on the geometry of arrangement of ions in the crystal. This constant α, called the *Madelung constant*, is 1·75 for NaCl and other crystals possessing NaCl structure. Thus, the lattice energy, U of the NaCl crystal is given by,

$$U = 1·75 e^2/r = -206 \text{ kcal mol}^{-1}$$

We note here again that if $\alpha = 1$, $U = -e^2/r$ which represents the attractive energy in an ion-pair. Thus, the energy in the ionic crystal is lowered by an additional 75 per cent (compared to the ion-pair). In all this discussion, we have assumed that lattice energy is due to coulombic attraction alone. However, because of the finite size of the electron cloud around ions, there would also be repulsive forces between ions and this generally decreases the lattice energy by about 10 per cent. In the case of NaCl, the true lattice energy is found to be -184 kcal mol^{-1}, a value which is still highly negative leaving no doubt that solid NaCl should be very stable.

In practice, lattice energies of ionic solids are obtained by employing energies involved in the various steps in the formation indicated earlier (this procedure is referred to as the *Born–Haber cycle*). Experimentally, the energy released in the formation of the solid is measured [corresponding to the net reaction Na(s) + $\frac{1}{2}$Cl$_2(g) \rightarrow$ NaCl(s)] and from this the experimental energies corresponding to steps 1 to 4 are subtracted (i.e. $U = \Delta E_{form} - \Delta E_{sub} - \frac{1}{2}D$ $-$ IE $-$ EA). This difference gives the 'experimental' lattice energy.[*] Lattice energies (in kcal mol^{-1}) of some alkali halides are listed below:

NaF 216	NaBr 176	LiCl 201	RbCl 162
NaCl 184	NaI 163	KCl 167	CsCl 156

Since ionic bonds are fairly strong, ionic solids, just like covalent solids, are generally hard (but brittle) and have high melting points. Most ionic solids are insulators at low temperatures just like covalent solids. However, in the molten or fused state, ions become free to move and in the fused state, ionic substances conduct electricity. The mobility of ions is also the reason for electrical conduction in solutions of these compounds (see Chapters 11 and 12). Ionic compounds dissolve in solvents of high dielectric constant, since the *coulomb force* ($F = q_1 q_2/Dr^2$, where q_1 and q_2 are two charges at distance r and D is the solvent dielectric constant) becomes weaker in these solvents.

7.2.3 Molecular Solids

In a molecule like hydrogen, the bonding capacity of both atoms is saturated and the molecule has no residual capacity for further bonding. However, weak attractive forces do exist between two or more hydrogen molecules which are responsible for the condensation of hydrogen gas at lower temperatures. Because the forces are weak, such substances liquefy or solidify at very low temperatures; that is, such substances have low melting and boiling points. In the condensed phases, molecules retain their identity since intramolecular forces are very much stronger than intermolecular forces and molecules, therefore, remain as discrete units in molecular solids.

The explanation of the weak attractive force is as follows. Even in non-polar molecules, there is a momentary imbalance of charge distribution. This

[*]This would be different from the coulombic energy. In the calculation of the energy of formation of NaCl discussed earlier, we employed the coulombic energy for lattice energy only as a first approximation. We should have actually used the lattice energy of 184 kcal mol^{-1} instead of the coulombic energy of 206 kcal mol^{-1}.

(a)   (b)   (c)

—— Attraction
------ Repulsion

(d)

—— Attraction
------ Repulsion

(e)
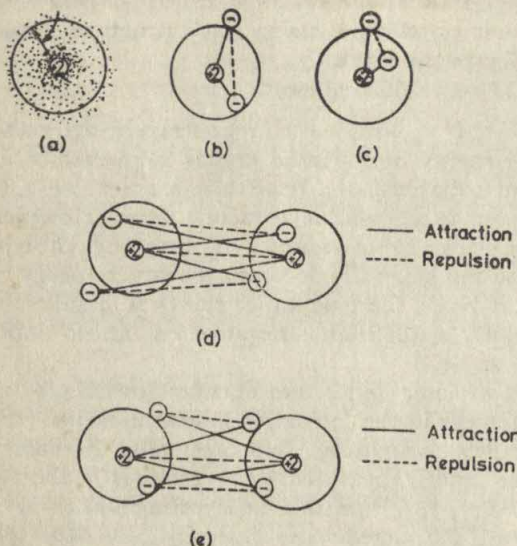
Fig. 7.4 van der Waals interaction between two helium atoms: (*a*) shows the electron cloud of a helium atom; (*b*) and (*c*) show two instantaneous locations of the two electrons (in both these configurations, helium atom has a transient dipole moment); (*d*) and (*e*) illustrate two of the infinite number of possible mutual configurations of the two helium atoms which are responsible for van der Waals forces.

is due to the fact that electron motion is not perfectly correlated and there is a small probability of occurrence of configurations in which the electron distribution is not symmetrical. The instantaneous imbalance creates a transient dipole which attracts similar dipoles in neighbouring molecules with a weak force (Fig. 7.4). This force is usually called *van der Waals force* and it operates even between inert gas atoms. As mentioned earlier, van der Waals forces are responsible for holding layers of graphite together. Similarly, the strands or chains of many polymers are held together in solid state by van der Waals interaction with other chains. For a more detailed discussion of intermolecular forces the reader is referred to Chapter 8 (particularly section 6).

Molecular crystals as a rule are soft with low melting points and high vapour pressures.

7.2.4 Metals

Nearly eighty elements exist as metals at normal temperatures and pressures. The metallic state is characterised by a number of common properties. All *metals* are good conductors of heat and electricity; they are generally strong but deformable, and exhibit shiny lustre when polished.

Metals differ from other substances significantly in terms of their electronic structure. In simple terms, a metal may be viewed as a collection of positive ions embedded in a ' sea ' of mobile electrons. Such a cloud of electrons, often referred to as electron gas, is considered to be responsible for the high electrical and thermal conductivity of metals. We can have a better understanding of the bonding in metals by applying the molecular orbital theory.

The MO theory of metals is commonly known as the *band model*. As in molecules, the bonding and anti-bonding MOs are formed from atomic orbitals of each atom. Since the smallest perceptible piece of a metal would typically contain about 10^{20} atoms, a large number of MOs are formed from the large number of atomic orbitals (AOs). The energies of the resulting MOs are so
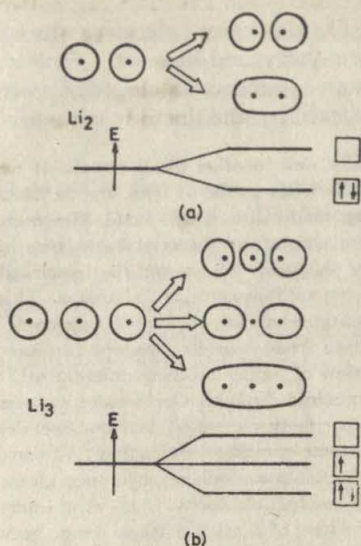
Fig. 7.5 (Left) Formation of molecular orbitals and the accompanying energy change in (a) Li_2 and (b) Li_3
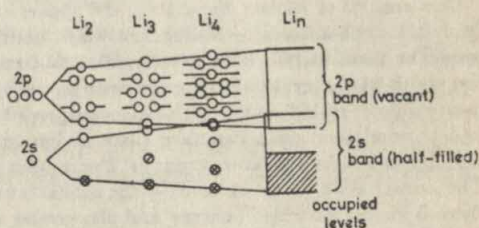
Fig. 7.6 Schematic band structure of lithium metal. See how the energy levels get closer as the number of lithium atoms increases. The $2p$ band of lithium metal is empty and the $2s$ band is half-full.

close to each other that they can almost be regarded as continuous. Such a group of energy levels is known as a band. The $1s$ atomic orbitals give rise to one band, the $2s$ atomic orbitals to another and so on. Usually, the various bands are separated by an energy gap—the so-called forbidden zone, but in metals some of the bands overlap.

Several important features of metallic bonding emerge when we consider an idealised one-dimensional lattice. Imagine the step-by-step formation of a chain of lithium atoms, Li-Li-Li...Li-Li-Li. The first step is the formation of Li_2 which is quite similar to the H_2 molecule. In Li_2 two molecular orbitals originate from the two $2s$ atomic orbitals of the lithium atoms, the two electrons (one each from the half-filled $2s$ AOs) occupying the lower energy MO leaving the other one vacant (Fig. 7.5a). Attaching another lithium atom yields the (hypothetical) linear Li_3 molecule (Fig. 7.5b). Here, the three AOs form three MOs. This process continues as the length of the chain increases, the number of MOs being equal to the number of AOs at each stage. For an array containing around 10^{20} lithium atoms, the MOs will be closely spaced with their energy varying nearly continuously. Since there are as many MOs as there are AOs (with each MO holding two electrons with opposite spins) and since $2s$ AO of each lithium atom has only one electron, it follows that half the MOs are fully occupied and the other half vacant. In other words, the $2s$ band in lithium is only half-filled. This conclusion remains valid if we consider a three-dimensional array of lithium atoms. Fig. 7.6 shows the schematic band structure of lithium metal; in the figure we have also shown the empty p orbitals. This figure clearly shows how the energy levels become closer as the number of lithium atoms in the system is increased.

This picture of metallic bonding readily explains metallic behaviour. Firstly, since the MOs are spread over the entire crystal, electrons in these MOs are completely delocalised. Secondly, the half-filled nature of the electron band means that electrons can be excited to these unoccupied states by appli-

cation of electric field thus permitting electrical conduction. The same two factors also account for thermal conductivity. The delocalised electrons absorb and re-emit light, rendering the metal surface shiny and lustrous. Finally, since the bonding electrons are not localised at any particular atom, the lattice can be deformed easily thus explaining the malleability and ductility of metals.

Our analysis of lithium band structure applies equally well to other alkali metals. If we apply the same analysis to magnesium which has two electrons in the $3s$ level, the $3s$ band would be predicted to be completely filled thus making magnesium a non-metal. However, the width of energy bands depends upon the crystal structure and the crystal structure of magnesium is such that the $3p$ band overlaps with the $3s$ band. This means that electrical and thermal conduction can take place and magnesium exhibits metallic behaviour. This example raises the obvious question—' Under what conditions can band overlap be expected ?' The answer is also quite obvious. If the orbital interaction (that is orbital overlap) increases there is greater lowering of energy and also greater overlap of bands involving different orbitals. Orbital interaction increases with decrease in internuclear distance. One way to shorten the internuclear distance is by applying pressure. Thus, many elements (even non-metals) under high pressure undergo phase transitions and become metallic (conducting). In fact, calculations show that at a pressure of a few hundred thousand atmospheres, hydrogen atoms should form a cubic close packed structure which should conduct electricity. Changes in internuclear separation can also occur when the crystal structure of a solid changes. Thus, grey tin which has a relatively open structure (density = 5·75 g/cc) is a non-metal, but the more densely packed white tin (density = 7·29 g/cc) is a metal. As long as the crystal structure of a metal is not disturbed, its band structure remains unaltered. This is why foreign atoms of the same valency and similar size can readily replace atoms in a metal in arbitrary proportions (forming alloys) without significantly altering the crystal structure or band structure.

7.2.5 Other Types of Bonding

The classification of solids into four major types should not be taken to imply that there is a sharp demarcation between one type and another. In some solids, more than one type of bonding is responsible for the stability of the structure. As mentioned earlier, van der Waals forces are responsible for inter-layer binding in graphite. Similarly, there are substances which form thread-like structures (e.g. amorphous sulphur, asbestos) where atoms are linked to one another along a chain by covalent bonds, but the chains are held together by weak van der Waals forces. In such substances, threads (or fibres) can be pulled out easily, but it is relatively harder to break threads. There are solids like the metal silicates where the bonding is partly ionic. Silicates form thread-type, sheet-type, or three-dimensional structures, held together by ionic interaction with cations present in them (see Chapter 16 for more details on silicate structures).

There are solids like ice which are held together by weak hydrogen bridges or hydrogen bonds (see Chapter 8, sections 7 and 8) formed between molecules (water molecules in the case of ice). Alcohols, carboxylic acids and amides also form hydrogen bonded crystals. In *proteins*, stable chains of atoms are formed by covalent as well as hydrogen bonds (see Chapter 18), but in the solid state the chains are held together by van der Waals forces.

7.3 CRYSTAL LATTICES

The diffraction of x-rays by crystals is a phenomenon of great importance to chemists since diffraction studies provide much of the structural information

on the arrangement of atoms, ions or molecules in crystals (see Chapter 4, section 8). From the x-ray diffraction patterns of crystalline solids, we can obtain the spacings between planes (containing the periodic ordered arrangement of atoms or other units constituting the solid) by applying *Bragg's law*:

$$n\lambda = 2d \sin \theta$$

Here, d is the spacing between two successive planes, λ the wavelength of x-rays, n an integer and θ the angle of the reflected (or incident) beam. These interplanar spacings are characteristic of a crystal and are determined by the size as well as the geometry of arrangement of atoms. X-ray diffraction patterns of crystals are therefore, like fingerprints and can be readily used to identify substances or analyse mixtures of substances. A typical diffraction pattern is shown in Fig. 7.7.
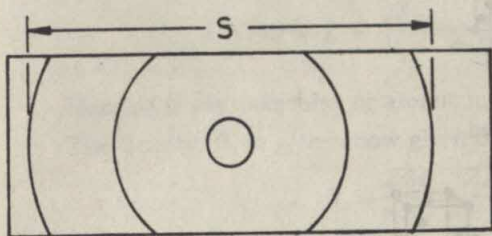
Fig. 7.7 Typical x-ray diffraction pattern of the powder of a crystalline substance. The diameter S of the rings is directly related to the dimensions of the unit cell.
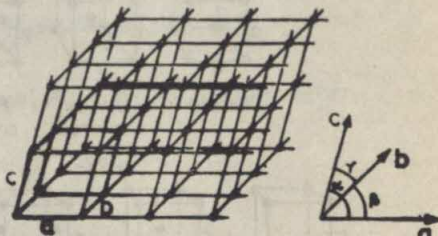
Fig. 7.8 A lattice. The three axes for translation are a, b and c and angles between axes are α, β and γ. The unit cell is the figure drawn by a thick line.

Crystals which give good x-ray diffraction patterns can be described in terms of regular three-dimensional arrays of points called *space lattices* (Fig. 7.8). A lattice is characterised by the distance between successive points along the three axes a, b and c shown in Fig. 7.8 and the angles between the axes, α, β and γ.

7.3.1 The Unit Cell

The unit cell is the smallest repeating unit in three dimensions which represents the entire crystal. The crystal may be considered to consist of a very large number of unit cells, each one in direct contact with its nearest neighbours and all similarly oriented in space. The unit cell of the lattice in Fig. 7.8 illustrates this point. Based on the various combinations of the lattice spacings along the three axes (a, b, and c) and the three angles (α, β, and γ), we can define seven *crystal systems* (Table 7.2). The simplest amongst these systems is the cubic, triclinic being the most complex one.

In the lattice, the points (atomic centres) may be assigned to the corners, face-centres or body-centres of the seven types of crystal systems listed in Table 7.2. In 1848, Bravais showed that there can be *only fourteen lattices* associated with the seven crystal systems depending on the distribution of atomic centres. For example, the cubic system can have three *Bravais lattices*. In Fig. 7.9 are shown the fourteen Bravais lattices. Every crystal possesses one of these lattice structures, but the detailed internal structure within the unit cell

Table 7.2 Different Crystal Systems

System	Axes	Angles	Examples
Cubic	$a=b=c$	$\alpha=\beta=\gamma=90°$	Cu,NaCl, CsCl, ZnS, CaF$_2$
Tetragonal	$a=b; c$	$\alpha=\beta=\gamma=90°$	White tin, SnO$_2$, TiO$_2$ (rutile)
Orthorhombic	$a; b; c$	$\alpha=\beta=\gamma=90°$	Rhombic sulphur, TiO$_2$ (brookite)
Monoclinic	$a; b; c$	$\alpha=\gamma=90°; \beta$	Monoclinic sulphur
Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma$	Calcite (CaCO$_3$)
Hexagonal	$a=b; c$	$\alpha=\beta=90°; \gamma=120°$	Graphite, BN, ZnS (Wurtzite)
Triclinic	$a; b; c$	$\alpha; \beta; \gamma$	K$_2$Cr$_2$O$_7$

Simple   Body-   Face-
           centered   centered
CUBIC

Simple   Body-   End-   Face-
         centered   centered   centered
ORTHORHOMBIC

Simple   Body-   Simple   End-
         centered   centered
TETRAGONAL   MONOCLINIC

Rhombohedral   Triclinic   Hexagonal
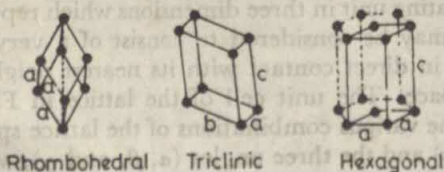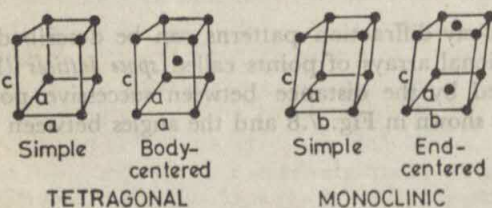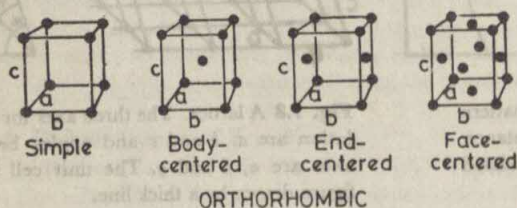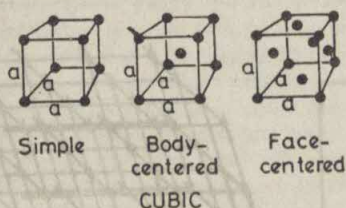
Fig. 7.9 Fourteen Bravais lattices: In the face-centered lattice, a lattice site is present at the centre of the face while in the body-centered lattice, the site is at the centre of the body. We readily see that triclinic lattice is the most complex one among the Bravais lattices, the cubic being the simplest.

will vary in complexity from substance to substance. Whatever be the complexity, the unit cell is the basic repeating unit in the crystal, and x-ray diffraction patterns directly provide the interplanar spacings (from Bragg's law) and hence the unit cell dimensions.* The structure within the unit cell is given by a detailed analysis of the intensities in the diffraction patterns.

*In cubic crystals, the interplanar spacing, d, is proportional to the length of the cube edge a_0; $d=a_0/K$ where K is a number that describes the orientation of the particular plane.

Having known the lattice of a crystal from x-ray diffraction studies, it is possible to determine the volume of the unit cell. In the case of the cubic unit cell, the volume, $v_c = a_0^3$ where a_0 is the cube edge. The density of the crystal is also the density D_c of the unit cell.

$$D_c = \text{DENSITY OF UNIT CELL} = \frac{\text{MASS OF UNIT CELL}}{\text{VOLUME OF UNIT CELL}} = \frac{m_c}{v_c}$$

The mass of the unit cell, m_c, is given by the total mass of the atoms or molecules in the cell.

$$m_c = Z \times m = (\text{NUMBER OF ATOMS OR MOLECULES}) \times (\text{MASS OF EACH ATOM OR MOLECULE})$$

Since the chemical composition of a substance is generally known, m_c value can be calculated provided the value of Z of the unit cell is known.

$$m_c = Z \times \frac{M}{N_0} = \frac{ZM}{6 \cdot 02 \times 10^{23}} = ZM \times 1 \cdot 66 \times 10^{-24}$$

Here M is the molecular or atomic mass and N_0 is the Avogadro number.

The density, D, in g/cc is now given by,

$$D_c = \frac{ZM}{v_c N_0} = \frac{ZM \times 1 \cdot 66 \times 10^{-24}}{v_c}$$

where v_c is in cc. By this method, we can readily calculate the density of a solid. However, since densities of most crystals are known or can be determined by the floatation method or the pyknometric method, we can employ the above method to determine the value of Z in the unit cell or the molecular mass of a substance. We must note here that Z is always an integer. The value of Z in cubic unit cells is discussed in the following sub-section. By taking a crystal whose density, crystal structure and molecular or atomic mass are known, we can determine the Avogadro number

$$Z = D_c v_c N_0 / M \text{ or } M = D_c v_c N_0 / Z \text{ or } N_0 = ZM / V_c D_c$$

7.3.2 Cubic Unit Cells

We shall now examine properties of the three cubic unit cells in some detail. Two questions can be asked about these unit cells. How many particles exist within the space of the unit cell? How many particles touch a given particle? We assign particles to the cubic unit cell on the following basis: (*i*) A particle in the corner of a cube is shared equally by all the unit cells that touch the same point. In two dimensions four squares can touch a given corner point; in three dimensions, eight cubes can touch a corner point. Therefore, one eighth of a corner particle belongs to a unit cell. (*ii*) A face particle can be shared by two cells and therefore one-half of face particle belongs to a unit cell. (*iii*) A body-centered particle belongs completely to the unit cell since it cannot be shared by any other unit cell.

The number of other particles touching a particle or the number of nearest neighbours of a particle is called the *coordination number*. The number of particles per unit cell, Z, and the coordination number in the three cubic cells are listed overleaf:

	Number of particles per unit cell	Coordination number
Simple cubic	$8 \times 1/8 = 1$	6
Body-centered cubic (BCC)	$(8 \times 1/8) + 1 = 2$	8
Face-centered cubic (FCC)	$(8 \times 1/8) + (6 \times 1/2) = 4$	12

We see that the coordination number as well as the number of particles is highest in the case of the face-centered cubic system. In fact, this arrangement is one of the two ways of arranging spherical particles in closest packing.* Metals like aluminium, copper, gold, silver, and nickel which crystallise in the FCC structure are highly malleable and ductile. Examples of metals in the BCC structure are tungsten, molybdenum, sodium, and barium and these metals are hard and brittle. Iron and some other metals exist in more than one structure (polymorphism or allotropy) depending on conditions of temperature and pressure.

It is instructive to assign coordinates to the various atoms (or lattice sites) in the three cubic unit cells with respect to the unit cell axes. If we assign the coordinates for an atom at the corner of the cube to be $(0, 0, 0)$, i.e. the corner point is taken to be the origin, then by a unit translation along any of the three axes (translation equivalent to the length of the cube edge in any of the three directions denoted by 1) we come back to an equivalent point. Therefore, only the atoms other than the corner atoms will have coordinates different from $(0, 0, 0)$. Following are the unique sets of coordinates possible in the cubic unit cells:

	Coordinates	Number of unique sets of coordinates
Simple cubic	$(0,0,0)$	1
Body-centered cubic	$(0,0,0)$ $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	2
Face-centered cubic	$(0,0,0)$; $(\frac{1}{2},\frac{1}{2},0)$; $(\frac{1}{2},0,\frac{1}{2})$; $(0,\frac{1}{2},\frac{1}{2})$	4

We see that the number of unique sets of coordinates in a cubic unit cell is exactly the same as the number of particles per unit cell calculated earlier.

Example 7.1 A compound formed of elements P and Q crystallises in the cubic structure where the P atoms are at the corners of a cube and Q atoms are at the body centres. What is the simplest formula of the compound?

P atoms are at the eight corners of the cube (each corner being shared by eight cubes). Therefore, number of P atoms in a unit cell $= 8 \times 1/8 = 1$
Q atoms are the body centres. Therefore, number of Q atoms in an unit cell $= 1$
The formula is PQ.

*The FCC packing is also called the cubic-closest-packing (CCP). The other close-packed arrangement is the hexagonal-closest-packing (HCP)—cadmium, titanium and zinc being typical examples. Packing arragements in crystals are discussed in some detail in the next section.

Example 7.2 An element exists in the body-centered cubic structure whose cell edge is 2·88A. The density of the element is 7·20 g/cc. How many atoms does 104 g of the element contain?

Volume of unit cell $= (2.88 \text{ A})^3 = 23.9 \text{ A}^3$
Volume of 104 g of the element $= 104 \text{ g}/7.20 \text{ g cc}^{-1} = 14.44 \text{ cc}$
Number of unit cells in this volume $= 14.44/23.9 \times 10^{-24}$
$= 6.04 \times 10^{23}$ unit cells

Each body-centered cube contains 2 atoms.
Therefore, the total number of atoms in 104 g is,
$2 \times 6.04 \times 10^{23} = 12.08 \times 10^{23}$ atoms

Example 7.3 A face-centered cubic solid of an element (atomic mass 60) has a cube edge of 4A. How would you calculate its density?

A face-centered cubic solid will have four atoms in the unit cell.

$$\text{DENSITY OF SOLID} = \text{DENSITY OF UNIT CELL} = \frac{\text{MASS OF UNIT CELL}}{\text{VOLUME OF UNIT CELL}}$$

$$= \frac{4 \times 60}{6.02 \times 10^{23} \times 4^3 \times 10^{-24}} = 6.24 \text{ gcc}^{-1}$$

7.3.3 Structures of Simple Ionic Compounds

It is much more difficult to describe the crystal structures or unit cells of compounds compared to those of elements. In the case of an element like copper (FCC), all the lattice points are occupied by copper atoms. However, if we were to consider the structure of the simplest ionic compound of the formula AB, we will have to describe the arrangement of both A and B ions. We shall now briefly examine the structures of a few simple ionic compounds of the type AB and AB_2.

O Cl   ● Cs   O Cl   ● Na   ● Zn   O S

CsCl   NaCl   ZnS
(Zinc Blende)
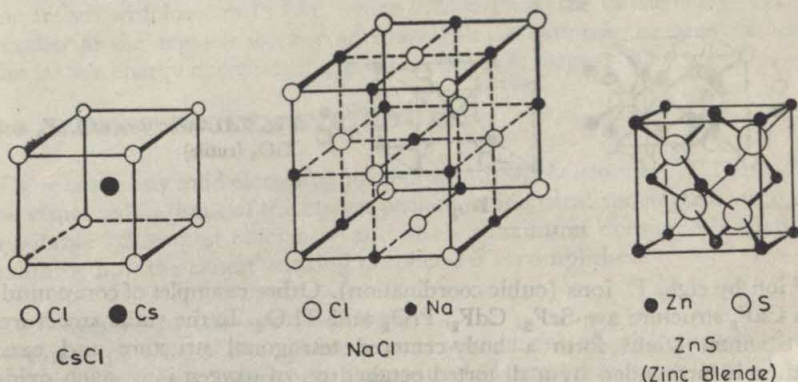
Fig. 7.10 CsCl, NaCl and ZnS—type cubic structures

Compounds of the type AB are generally cubic* and can possess one of three types of structures: cesium chloride (CsCl))type, rock salt (NaCl) type and zinc blende (ZnS) type (Fig. 7.10). These are described in Table 7.3.

*AB compounds can also crystallise in the hexagonal wurtzite (ZnS) structure, but we shall not consider this structure here.

Table 7.3   Three Types of Cubic Ionic Solids

Structure	Description and examples	Coordination number	Number of A B Units per unit cell
CsCl-type	Cs⁺ at the body centre of a cube of Cl⁻ and Cl⁻ at the centre of a cube of Cs⁺, e.g. CsCl, CsBr, CsI, TlCl	Cs⁺ 8 Cl⁻ 8	1
NaCl-type	Both Na⁺ and Cl⁻ form FCC lattices and the two interpenetrate each other half-way, e.g. all sodium halides, AgCl, transition metal monoxides	Na⁺ 6 Cl⁻ 6	4
ZnS-type	This also has a face centered arrangement of ions, but more complex than that of NaCl, e.g. ZnS, CuCl, HgS	Zn⁺² 4 S⁻² 4	4

Chlorides, bromides and iodides of lithium, sodium, potassium and rubidium (as well as some of the halides of silver), all of which ordinarily possess the NaCl structure with 6 : 6 coordination, transform to the CsCl structure with 8 : 8 coordination on application of pressure; notice that high pressure increases the coordination. On the other hand, CsCl on heating transforms to the NaCl structure at 490°C; similarly, NH_4Cl, NH_4Br and NH_4I transform from the CsCl structure to the NaCl structure at 184°, 138° and −18°C respectively.

Many of the compounds of the formula AB_2 crystallise in the cubic fluorite (CaF_2) type structure or the tetragonal rutile (TiO_2) structure (Fig. 7.11). In the CaF_2 structure, each F^- ion is coordinated by four Ca^{2+} ions and each

Ca O
F ●

Ti ●
O ○
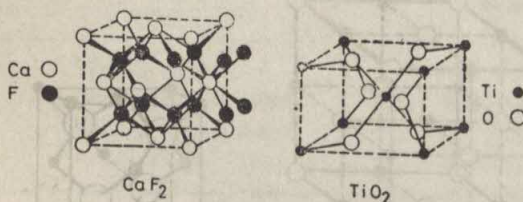
Fig. 7.11 Structures of CaF_2 and TiO_2 (rutile)

Ca F₂

TiO₂

Ca^{+2} ion by eight F^- ions (cubic coordination). Other examples of compounds with CaF_2 structure are SrF_2, CdF_2, PrO_2 and ThO_2. In the rutile structure, the titanium atoms form a body-centered tetragonal structure and each titanium is surrounded by a distorted octahedron of oxygen ions; each oxide ion is surrounded by three titanium ions (3 : 6 coordination). Typical examples of rutile phases are RuO_2, PbO_2 and MgF_2.

Structures of many of the ionic compounds can be understood in terms of the packing arrangements of ions (and the relative sizes of cations and anions) and we shall deal with this aspect in section 7.4.

7.3.4 Ionic Radii

X-ray measurements on ionic crystals provide dimensions of unit cells and distances between adjacent ions. We can obtain the radii of ions (assuming that they are spheres) from the dimensions of the unit cells. The unit cell

dimensions of crystals of NaCl structure suggest that anions and cations are of such size as to be in contact with one another. Further the unit cell dimensions of alkali metal halides vary in a regular manner with the halide and alkali metal ions. It is possible to assign radii to these cations and anions by suitably dividing the interatomic distance. We shall not elaborate the method of doing so here but will only list the radii of some of these ions obtained in this manner by Pauling.

Li^+	Na^+	K^+	Rb^+	Cs^+	Be^{2+}	Mg^{2+}	Ca^{2+}	Al^{3+}
0·60	0·95	1·33	1·48	1·60	0·31	0·65	0·99	0·5

F^-	Cl^-	Br^-	I^-	O^{2-}	S^{2-}	Se^{2-}	Te^{2-}
1·36	1·81	1·95	2·16	1·40	1·84	1·98	2·21

We see that there is good agreement between the calculated and observed values of interionic distances (in A) in ionic crystals as exemplified below:

	NaCl	KCl	RbCl	CsCl	NaI
Calculated (sum of radii)	2·76	3·14	3·29	3·50	3·15
Observed	2·81	3·14	3·29	3·47	3·23

The ionic radii listed above show the expected trends. The radius increases in a group with increase in atomic number. In the same period, the radius of isoelectronic ions decreases with the charge of the ion (e.g. Na^+, Mg^{2+} and Al^{3+}). As will be shown later, ionic radii of anions and cations determine the coordination number and packing in ionic solids. Lattice energies show interesting trends with ionic radii (see section 7.2.2). Thus, the lattice energy becomes smaller as the negative ion becomes larger (if the cation is the same); similarly, the lattice energy decreases if the cation becomes larger.

7.4 CLOSEST-PACKED STRUCTURES

There are many solid elements and compounds whose atomic arrangements can be visualised in terms of the closest packing of identical spheres so as to use the available space most efficiently and attain maximum density. We shall now examine how the closest packing of spheres is accomplished.

7.4.1 Sphere in Closest Packings
A closest packing of like spheres is an arrangement of spheres which permits each sphere to be in intimate contact with the largest number of its neighbours.

Fig. 7.12 Two-dimensional packing of spheres: (a) in a square lattice and (b) in a triangular lattice. In two dimensions, a sphere becomes a circle of area πR^2 where R is the radius of the sphere. The arrangement in (b) represents the closest packing possible.
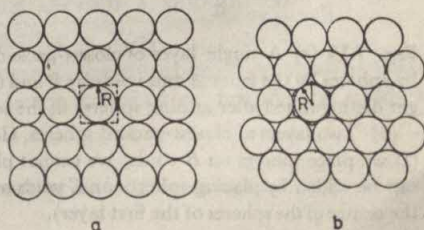
For spheres of equal size, this means that each sphere would have six nearest neighbours in a closest-packed layer and twelve in a three-dimensional closest packing. Fig. 7.12(a) shows a layer of spheres arranged on the points of a square lattice. The efficiency of this arrangement, where the area belonging to each circle is a square, is calculated as follows:

$$\text{EFFICIENCY} = 100 \times \frac{\text{AREA OF A CIRCLE}}{\text{AREA OF A SQUARE}} = \frac{\pi R^2}{4R^2} = \frac{\pi}{4}$$

$$= 78 \cdot 5 \text{ per cent}$$

A layer of spheres arranged on the points of a triangular lattice is shown in Fig. 7.12(b). The area associated with a circle here is a hexagon and each hexagon comprises of twelve right-angled triangles. The area of a right-angled triangle is $(R/2)(R/\sqrt{3}) = R^2/2\sqrt{3}$. The area of a hexagon is, therefore, $12 \times R^2/2\sqrt{3} = 2\sqrt{3}\, R^2$.

$$\text{EFFICIENCY} = 100 \times \frac{\text{AREA OF A CIRCLE}}{\text{AREA OF A HEXAGON}} = \frac{\pi R^2}{2\sqrt{3}\, R^2} = 90 \cdot 7 \text{ per cent}$$

The packing arrangement in Fig. 17.12 (b) represents the most efficient way of occupying space and this layer is called *a hexagonal closest-packed layer*.

In the two-dimensional hexagonal closest-packed arrangement of spheres, each sphere is surrounded by six others (nearest neighbours). Let us label each occupied site in the layer with letter A as shown in Fig. 7.13(a). The second layer of closest-packed spheres can be added by placing spheres in the depression or voids (or holes) of the first layer. We shall label these voids by letters B and C (Fig. 7.13a). If we place a sphere at voids labelled B we cannot place any spheres at the C voids and vice versa. In Fig. 7.13(b) is shown the closest-packed arrangement obtained by packing spheres on B voids. The third layer can now be added by placing spheres on the voids marked C or the A voids created by the second layer. If we place the spheres on C, we get the stacking sequence ABC and if we place them on A, we get the stacking sequence AB. These two sequences can be repeated indefinitely to get the $ABCABCABC...$

a   b
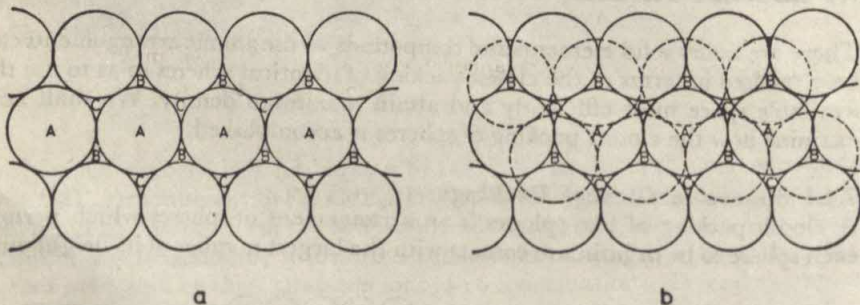
Fig. 7.13 (a) A single layer of closest-packed spheres. Here we have marked sites occupied by spheres by the letter A and voids by B and C. B and C voids are exactly identical, but they get distinguished after adding spheres in the second layer as shown in (b).

(b) Two layers of closest-packed spheres. Here, we have placed spheres on all the B voids. (If we place spheres on B voids, we cannot place any on the C voids.) Now the third layer can be added by placing spheres on C voids or A voids (formed by the second layer right at the centre of the spheres of the first layer).

and *ABABAB*... arrangements; these are respectively called the *cubic closest packing* (CCP) and *hexagonal closest packing* (HCP) arrangements respectively. Both these are equally efficient with 74 per cent of the available volume occupied by spheres. In both CCP and HCP structures, the coordination number of a sphere remains twelve. In the CCP arrangement, there is always a sphere at each face centre of a cube and CCP is, therefore, also called the face-centered cubic arrangement. Noble gases as well as many metals crystallise in either of these closest-packed arrangements (see section 7.3 for examples). In addition, metals also crystallise in the body-centered cubic structure which is not a closest-packed arrangement. This arrangement has a coordination number of eight and only 68 per cent of the total volume is occupied by spheres. Solid hydrogen has the CCP structure since the electron cloud is essentially spherical in hydrogen molecule; hydrogen halides, however, crystallise in the HCP structure.

7.4.2 Voids in Closest-packed Structures

Two kinds of voids occur in closest packings. If a triangular void in a closest packed layer has a sphere over it, we get a void with four spheres around it as

Fig. 7.14 (a) A tetrahedral void; (b) the four spheres surrounding a tetrahedral void are present at the corners of a tetrahedron; and (c) coordination polyhedron of a tetrahedral void (only those parts of the four spheres that belong to a tetrahedral void are shown)
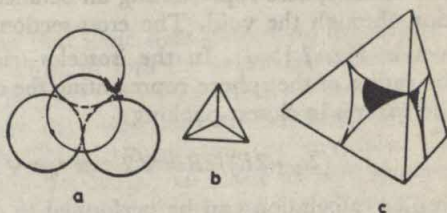
shown in Fig. 7.14(a) and (b), and such a void is called a *tetrahedral void*. In Fig. 7.13(b), the B voids (over which we placed the second layer spheres) are tetrahedral voids. The coordination number of a tetrahedral void is four (Fig. 7.14c). If a triangular void pointing up in one closest-packed layer is covered by a triangular void pointing down in the next layer as shown in Fig. 7.15(a), then the void is surrounded by six spheres arranged on the corners of an octahedron (Fig. 7.15b); such a void is called an *octahedral void*. The coordination number of an octahedral void is six as shown in Fig. 7.15(c). In Fig. 7.13(b), the C voids, after the addition of the second layer, represent octahedral voids.

The number of octahedral voids belonging to one sphere is given by the ratio,

$$\frac{\text{NUMBER OF OCTAHEDRAL VOIDS AROUND A SPHERE}}{\text{NUMBER OF SPHERES AROUND A VOID}} = \frac{6}{6} = 1$$

The number of tetrahedral voids belonging to a sphere is given by the ratio,

$$\frac{\text{NUMBER OF TETRAHEDRAL VOIDS AROUND A SPHERE}}{\text{NUMBER OF SPHERES AROUND A VOID}} = \frac{8}{4} = 2$$

We see that in a closest-packed arrangement, the number of octahedral voids is equal to the number of spheres while the number of tetrahedral voids is double the number of spheres.*

*It is advisable for students to obtain this result by actually counting the number of voids of each kind around a sphere.

The radii of the voids (interstitial sites) in closest-packed structures are related to the sizes of the spheres present in the structures. We can readily calculate the radius of the sphere representing an octahedral void by considering the cross-section through the void. The cross-section of the octahedron is a square as shown in Fig. 7.15(d). In the isosceles triangle ABC, $(AB/AC) = \sqrt{2/1}$. If r_0 is the radius of the sphere representing the octahedral void and R is the radius of the spheres in closest-packing,

$$(2r_0 + 2R)/2R = \sqrt{2} \quad \text{or} \quad r_0 = \sqrt{2}R - R = 0.414R$$

A similar calculation can be performed to determine the radius of the sphere representing a tetrahedral void. The radius of this void, r_t, turns out to be $0.225R$. From this discussion we see that in order to occupy an octahedral void (without in any way disturbing the closest-packed structure), the radius of the small sphere should not be greater than 0.414 times the radius of the large spheres forming the closest-packed structure. A tetrahedral void is much smaller than an octahedral void and spheres that can occupy tetrahedral voids should therefore, be of much smaller radius.

7.4.3 Structures of Substances Related to Closest-packed Lattices

Besides noble gases and metals which crystallise in closest-packed structures, a large number of inorganic compounds have structures related to closest packings. In such compounds one kind of ion forms the closest-packed structure while another kind of ion goes into the voids. In many of the solid solutions of metals similarly some of the atoms are present in the voids. Properties of materials are often affected when foreign impurities or some of the atoms comprising the material itself are present as interstitial atoms in the voids; such interstitials are an important kind of imperfection in solids (see section 7.5).

From the description of the closest-packed structures, we can draw some inferences regarding the structures of simple compounds. For example, if in a compound of the general formula AB, the B ions form a closest-packed lattice, then A ions of opposite charge can occupy all the octahedral voids or one-half of the tetrahedral voids. If the formula of the compound is A_2B, all the tetrahedral sites will be occupied by A ions. Typical descriptions of ionic solids forming nearly close-packed structures are given in

Table 7.4. It must be remembered that these descriptions are not exact in the sense that some of these ionic compounds are not strictly the closest-packed structures. For example, in NaCl the ions along the diagonal of the cube face do not touch each other.

An interesting case of packing is given by the oxides of iron, FeO, Fe_2O_3 and Fe_3O_4. FeO has the rock-salt (NaCl) structure and ideally Fe^{2+} ions should occupy the octahedral voids. However, this oxide is always non-stoichiometric and the composition is generally $Fe_{0.95}O$ (wustite). We can obtain this composition if a small number of Fe^{2+} ions are replaced by two-thirds as many Fe^{3+} ions in the octahedral voids. If we convert two-thirds of the Fe^{2+} ions in FeO into Fe^{3+} ions, we get the composition, $FeO \cdot Fe_2O_3$ or Fe_3O_4 (*magnetite*); in Fe_3O_4, all the Fe^{2+} ions are in octahedral voids and the Fe^{3+} ions are equally distributed between octahedral and tetrahedral voids. This is the well-known *inverse spinel structure*; another example of this structure is $MgFe_2O_4$ where Mg^{2+} ions replace Fe^{2+} ions of Fe_3O_4. In the *normal spinel structure* of compounds of the general formula AB_2O_4 (e.g. *ferrites* like $ZnFe_2O_4$, $MgAl_2O_4$), the divalent A^{2+} ions are in tetrahedral voids and the trivalent B^{3+} ions are in octahedral voids. Fe_2O_3 may be visualised as $Fe_{0.67}O$ which can be formed by the replacement of all the Fe^{2+} ions (in FeO) by two-thirds as many Fe^{3+} ions. Many of the *ferrites* which possess spinel-type structures are important magnetic materials used as pot cores in telephones or memory loops in computers.

We see from the earlier discussion that ionic sizes determine the nature of packing in close-packed structures. Thus, in ZnS the small Zn^{2+} ions occupy half the tetrahedral voids while the large S^{2-} ions form the close-packed lattice. In NaCl, on the other hand (where the ionic sizes are similar), Na^+ ions occupy the octahedral voids while Cl^- ions form the CCP structure. The coordination number of an ion (or an atom) in close-packed structures depends on the ratio of its radius with respect to the radius of the ions or atoms surrounding it. In the case of ionic solids, this *radius ratio* is the ratio (r^+/r^-) of the cation radius to the anion radius. Cations and anions get as close to each other as allowed by the respective radii to have maximum coulomb attraction, but anions never approach each other more closely than permitted by the ionic radii. Cations tend to get surrounded by the largest possible number of anions and, therefore, the larger the radius ratio, the larger is the coordination number of the cation. As we have seen already, only tetrahedral coordination is possible when the radius ratio is in the range 0·225–

Table 7.4 Descriptions of Ionic Solids

Compound	Ions forming the closest-packed structure	Ions in voids	Coordination number, CN^1	Other examples
NaCl	Cl^- forms CCP structure	Na^+ in all octahedral voids	6 : 6	Halides of Li, Na, K and Rh; AgCl, AgBr; CaO; MgO; TiO
ZnS	S^{2-} forms CCP structure	Zn^{2+} in alternate tetrahedral voids	4 : 4	CuCl; CuBr; CuI; BeS
CaF_2	Ca^{2+} forms CCP structure	F^- in all tetrahedral voids	8 : 4	SrF_2; HfO_2; UO_2
Na_2O	O^{2-} forms CCP structure	Na^+ in all tetrahedral voids	4 : 8	Li_2O; K_2S; Rb_2S

[1] Note that CN of octahedral and tetrahedral voids are six and four respectively.

Table 7.5   Radius Ratios and Coordination Numbers

Range of radius ratio	CN	Geometry	Example	Range of radius ratio	CN	Geometry	Example
-0.155	2	linear	HF^-_2(Bifluoride ion)	0.414–0.732	6	Octahedral	NaCl type solids
0.155–0.225	3	triangular	BO^{3-}_3, BN	0.732–1.0	8	Cubic	CsCl, CsI
0.225–0.414	4	tetrahedral	SiO^{4-}_4, ZnS type cubic solids	1.0	12	Closest sphere packing	

0.414, but octahedral coordination becomes possible above a radius ratio of 0.414. In Table 7.5 we have summarised the range of radius ratios over which coordination numbers of 2, 3, 4, 6, 8 and 12 are likely to be stable. By employing values of ionic radii (see section 7.2) for cations and anions, it is possible to predict the coordination number of cations in compounds. Radius ratio is indeed a useful concept for the prediction of structures of ionic compounds.

7.5 HEAT CAPACITY OF SOLIDS

The important thermal properties of solids are heat capacity, thermal conductivity and thermal expansion.   Thermal expansion can be understood in terms of the variation of average interatomic distances with temperature. Heat capacity and thermal conductivity are both governed by characteristic lattice vibrations as well as elecronic contributions.

Dulong and Petit proposed an empirical law according to which the heat capacity (C_v) of a solid element is approximately 6·3 cal/mol deg. Experiments show that this law holds for many solid elements and compounds, but the heat capacity itself is a function of temperature (Fig. 7.16). At 0 K, heat capacity of all substances becomes zero, and the value of 6·3 cal/ deg is the limiting value at relatively high temperatures. Einstein, employing quantum theory, showed why the heat capacity should decrease at low temperatures, but the decrease was too rapid. Debye later provided a satisfactory theoretical treatment which indicated that C_v should have a T^3 dependence at low temperatures; this has been verified experimentally (see Chapter 9). The variation of heat capacity with temperature discussed till now arises from the contribution from lattice vibrations. In addition to this, there will also be contributions from conduction electrons to the low-temperature heat capacity of metals and this term is proportional to T. Thus, the low-temperature specific heat is given by, C_v (lattice) $+ C_v$ (electronic) $= \alpha T^3 + \beta T$.

Fig. 7.16 Heat capacity of silver as a function of temperature

7.6 IMPERFECTIONS IN SOLIDS

In crystals, the state of complete order and of lowest energy is found at absolute zero of temperature. At any temperature above 0 K there will be some depar-

ture from complete order. In principle, any deviation from a completely ordered arrangement in a crystal constitutes native disorder. In addition, crystals may have disorder due to the presence of impurities. The term *imperfection* or *defect* is generally employed to denote a departure from a perfectly periodic array of atoms in a crystal, immaterial of whether the imperfection is intrinsic or extrinsic in origin. Many a property of a solid such as the electrical conductivity, optical spectra or mechanical strength cannot be explained on the basis of its crystal structure alone. Imperfections may not only change the properties of a crystal, but also give rise to certain new properties of interest.

The important types of native disorder are those associated with *atomic and electronic imperfections*. In addition, *orientational disorder* and *motional disorder* are also found in certain solids. A typical example of orientational disorder is found in ferromagnetic solids where all the magnetic moments are aligned in a magnetic field at low temperatures. At higher temperatures, the solid becomes paramagnetic due to the disorientation of the magnetic moments. Motional disorder is exemplified by ammonium halides where the ammonium ions rotate in phase at low temperatures. At higher temperatures the ions rotate out of phase. In this section, we shall be limiting our discussion mainly to the two more important types of native disorder arising from electronic and atomic imperfections.

7.6.1 Electronic Imperfections

It may appear strange at first sight to consider electrons in solids as imperfections, but we will soon see that such a classification is helpful in understanding several phenomena. In perfect covalent or ionic crystals at 0 K, electrons are present in the fully occupied lowest-energy states. The distribution of the valence electrons depends on the nature of the chemical bonds in the case of covalent crystals while they are mainly concentrated about the electronegative component in ionic crystals. In both these cases, electrons do not move under an applied electric field. Above 0 K, some of the electrons may occupy higher energy states depending on the temperature and the energy. distribution in the allowed states. Thus, in crystals of pure silicon, some electrons are released thermally from the covalent bonds at temperatures above 0 K. These electrons which are free to move in the crystal would be responsible for the electrical conductivity in silicon. The electron deficient bond produced by the removal of an electron is referred to as a *positive hole* or *hole*. Holes also give rise to electrical conductivity, but the direction of motion of the holes in an electric field will be opposite to that of the electrons. Excited electrons and holes in solids are considered to be electronic imperfections. Electrons and holes are generally designated by e and h respectively and their concentrations by n and p. The equilibrium concentrations of holes and electrons will be equal in pure crystals of silicon and germanium. Electrons and holes can be preferentially produced in these covalent crystals by adding suitable impurities as will be discussed later.

Germanium and silicon being group IV elements, have a characteristic valence of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combinations of elements of groups III and V or II and VI to simulate the average valence of four as in Ge or Si. Typical of groups III–V compounds are InSb, AlP and GaAs; ZnS, CdS, CdSe and HgTe are examples of groups II–VI compounds. In these compounds

the bonds are not perfectly covalent and the ionicity will vary depending on the relative electronegativities of the two component elements. The groups III–V and groups II–VI compounds exhibit interesting electronic (electrical and optical) properties which have been exploited in the electronics industry.

In most ionic solids electrons are localised on a particular ion (unlike in metals where electrons are delocalised). The concept of electrons and holes can be employed in ionic crystals just as in covalent solids. This is best understood by considering an ionic crystal where cations of two different valence states can be present. Consider a solid containing mainly ferrous ions. If we introduce a small number of Fe^{3+} ions in this solid, it is equivalent to introducing holes. This is because, Fe^{3+} ions have one electron less than the preponderant Fe^{2+} ions in the solid. In such a solid, the electrons and holes spend appreciable time at cation sites before ' hopping ' to the adjacent sites. The hopping process may be visualised in terms of the change, Fe^{2+} Fe^{2+} Fe^{3+} $Fe^{2+} \rightarrow Fe^{2+}$ Fe^{3+} Fe^{2+} Fe^{2+}. The hopping process is responsible for the electrical conduction in such solids.

7.6.2 Atomic Imperfections

If imperfections in a crystal are caused by a departure from the periodic arrangement in the vicinity of an atom or a group of atoms, the imperfections are called *point defects*. If the deviations from periodicity extend over microscopic regions of the crystal, they are referred to as *lattice imperfections*. Lattice imperfections may extend along lines (*line defects*) or surfaces (*plane defects*). Line defects are also called *dislocations*. The various types of atomic imperfections in crystals are listed in Table 7.6.

Point defects: When an atom is missing from its normal lattice site, a lattice vacancy (*Schottky defect*) is created. In stoichiometric ionic crystals, a vacancy of one ion is accompanied by the creation of a vacancy of the oppositely charged ion in order to maintain electroneutrality (Fig. 7.17). Thus, equal numbers of cation and anion vacancies are found in alkali halides. In NaCl, there are approximately 10^6 Schottky pairs per cc at room temperature; in one cc there are about 10^{22} ions and, therefore, there will be one Schottky defect for 10^{16} ions. Presence of a large number of Schottky defects in a crystal, lowers its density markedly. The pyknometric density of vanadium monoxide, VO, is

a   b   c
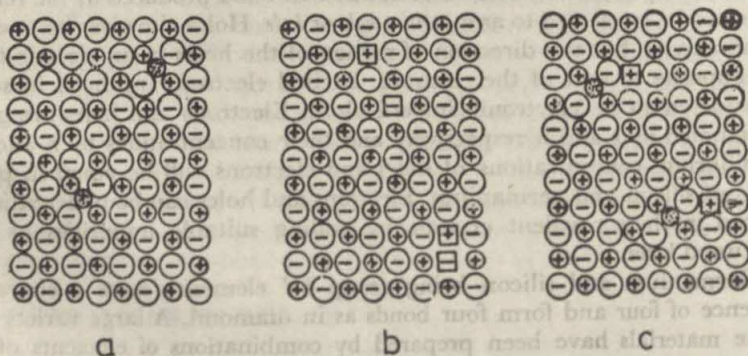
Fig. 7.17 (*a*) Interstitials, (*b*) Schottky defects and (*c*) Frenkel defects in ionic solids. Squares represent vacancies and shaded circles represent interstitials.

5·6 g/cc while the x-ray density (determined from the unit cell dimensions, as described in section 7.3.1) is 6·5 g/cc. Obviously, there is about 15 per cent disorder of the Schottky kind in VO.

Atoms (or ions) which occupy the normally vacant interstitial sites in a crystal are called *interstitials*. The important factor determining the formation of interstitials is the size of the atom, since they generally go into the voids discussed earlier in section 7.4.2. There is another kind of point defect called the *antistructure* disorder, where atoms occupy sites which in the ideal crystal are assigned to atoms of a different kind. In a crystal containing atoms X and Y, some of the X atoms occupy Y sites and an equal number of Y atoms occupy X sites, if there is antistructure disorder in the crystal. Antistructure disorder is commonly found in alloys, particularly at higher temperatures, but is rare in ionic crystals since it would bring like ions next to each other.

In addition to the three basic types of point defects (Schottky, interstitial and antistructure) discussed above, three hybrid type of defects can arise from combinations of any two of the basic types. Of these three combinations, the *Frenkel defects* are more common in ionic solids. In Fig. 7.17, Frenkel defects are shown along with the Schottky defects and interstitials. In pure alkali halides one does not encounter Frenkel defects since the ions cannot get into the interstitial sites. Frenkel defects are however found in silver halides where

Table 7.6 Atomic Imperfections in Crystals

Imperfection	Nature of imperfection
POINT DEFECTS	
Schottky defect	Atom missing from the normal lattice site creating a vacancy
Interstitial	Atom in a normally vacant interstitial site
Antistructure	Atoms misplaced wrongly in sites assigned for some other atoms
Frenkel defect	Atom in the lattice site displaced to an interstitial site creating a vacancy
LINE DEFECTS	
Edge dislocation	Dislocation line marks the edge of an extra plane of atoms which is inserted part way in a crystal
Screw dislocation	Displacement of atoms in one part of a crystal relative to the rest of the crystal causes a spiral around the dislocation line
PLANE DEFECTS	
Grain boundary	Boundary between two crystals in a polycrystalline solid
Stacking faults	Boundary between two layers with different stacking sequences in close-packed structures
Shear structures	Structures where excess atoms are present in folded planes connecting slabs of the crystal of normal structure

the Ag⁺ ions are considerably smaller than the halide ions. Unlike Schottky defects, Frenkel defects do not change the density of the solid. In many real systems, various types of point imperfections may occur simultaneously. Thus

in NiAl, Schottky defect and antistructure disorder are known to be present; in AgBr Schottky and Frenkel defects coexist.

There is a large variety of non-stoichiometric inorganic solids which contain an excess or deficiency of one of the components. Such solids showing deviations from the ideal stoichiometric composition form an important group of defect solids. There are some solids which are difficult to prepare in the stoichiometric composition; thus, the ideal composition in compounds like FeO is metastable (normally we get $Fe_{0.95}O$). The most stable compositions of praseodymium and terbium oxides under ordinary conditions are Pr_6O_{11} and Tb_4O_7 respectively. Similarly, many of the groups II–VI compounds, such as ZnO and CdS, are difficult to prepare in their stoichiometric compositions. In fact, compounds become more interesting to a solid state chemist when there is non-stoichiometry. In certain solids, gross variations in composition are also accompanied by changes in crystal structure, while in some others marked deviations from the stoichiometric composition may occur without any change in crystal structure. Thus, VO and TiO can be prepared over a range of compositions (VO_x or TiO_x, $x \approx 0.6–1.3$) with NaCl structure.

Zinc oxide loses oxygen reversibly at high temperatures and turns yellow in colour. The excess metal is accommodated interstially, giving rise to electrons trapped in the neighbourhood. The enhanced electrical conductivity of the non-stoichiometric ZnO arises from these electrons (n-type conduction). In FeO, the *non-stoichiometry* arises from an excess of anions and the electrical conductivity is due to positive holes (p-type conduction). In such oxides, the deviation from stoichiometry is accommodated by the change in the valence state of the cation; the cation valency decreases if there is metal or cation excess while the cation valency increases if there is anion excess. These two behaviours of oxides can be understood in terms of the basic chemical reactions of the type given below:

Oxygen (anion) excess : $\frac{1}{2} O_2(g) \rightleftharpoons O^{-2}(s) + $ cation vacancy $+ 2\,h$ (p type)

Oxygen (anion) deficiency: $O^{-2}(s) \rightleftharpoons \frac{1}{2}O_2(g) + $ anion vacancy $+ 2e$ (n type)
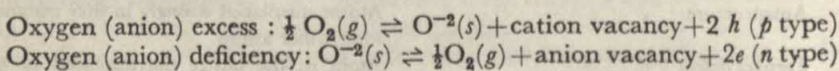
Anion vacancies in alkali halides are readily produced by heating the alkali halide crystals in an atmosphere of the alkali metal vapour. When the metal atoms deposit on the surface of the alkali halide crystal, halide ions diffuse into the surface and combine with the metal atoms. The electrons produced by the ionisation of the alkali metal atoms then diffuse into the crystal and combine with a negative ion vacancy. Electrons trapped in anion vacancies (referred to as *F centres*) give rise to interesting optical and electrical properties. Thus, excess potassium in KCl makes the crystal appear violet and excess lithium in LiCl makes it pink. Alkali halides with holes trapped in cation vacancies (*V centres*) can be produced by heating the alkali halides in an atmosphere of the halogen. Such colour centres can also be produced by the irradiation of alkali halides by high energy radiation like x-rays or γ-rays.

Till now, the discussion of point defects has been limited to systems where there were no foreign atoms or impurities. Foreign atoms can occupy either interstitial or substitutional sites in a host crystal. The electronic structure of the impurity is of importance in the case of substitutional solid solutions while the size of the impurity atom determines the formation of interstitial solid solutions. Many of the impurity systems provide new and interesting

properties of great importance; the most well-known of such solid solutions are those of group III or group V impurities with group IV elements like Ge or Si. Group III elements like Ga or Al and Group V elements like P or As enter Ge or Si substitutionally (Fig. 7.18). Group V elements will have one excess valence electron after forming the four covalent bonds normally formed by group IV elements. The excess electrons may be released to move through the host structure by thermal energies to give rise to n type conduction. A group III element which has only three valence electrons creates one electron-deficient bond giving rise to a hole which can move in the crystal carrying an effective positive charge. The electrical conductivity will therefore be of p type. In solid

Fig. 7.18 Introduction of holes (h) into silicon by the addition of group III impurity (Al) and of electrons (e) by the addition of group V impurity (P)

solutions of group IV elements with either group V or III elements, the overall charge neutrality is maintained. The impurities in these cases are ionised; imperfections that ionise releasing electrons (e.g. P or As in Ge or Si) are called *donors* while those which ionise by accepting electrons (e.g. Ga or Al in Ge or Si) are called *acceptors*.

The magnitude of energy required to ionise impurity atoms is generally small and in germanium at ordinary temperatures ($kT \approx 0.025$ ev) nearly all the donor and acceptor levels are ionised. The ionisation energy decreases with the increase in impurity concentration and if the concentration is sufficiently high, a large fraction of ionised donors and acceptors is found even at low temperatures. The extra electron of the donor atom may be visualised as moving in orbits in the field of a positive charge. The picture is somewhat similar to that of the hydrogen atom, the main difference being that the electron and the positive charge are in a medium of high dielectric constant. Further, the radius of the orbit is much larger covering several atomic distances.

A common method of introducing defects in ionic solids is by adding impurity ions. If the impurity ions are in different valence state from that of the host ions, vacancies are created. Literature abounds in examples where interstitials or vacancies are produced by addition of impurities to ionic solids. For example, addition of $CdCl_2$ to AgCl or $SrCl_2$ to NaCl yields solid solutions where the divalent cations occupy the Ag^+ or Na^+ sites and produce cation vacancies equal in number to that of the divalent ions (Fig. 7.19a). If one adds a molecule of a rare earth fluoride, MF_3, to CaF_2, the type as well as the concentration of defects produced will depend on the valence state of the rare earth ion in the host lattice. If the rare earth ion is in the $+3$ state, one F^- interstitial will be formed beside a new cation site; if the rare earth ion is in the $+2$ state there will be no interstitial F^- ion.

If the ions in a host crystal can assume two or more valence states, addition of an impurity ion in a valence state different from the normal valence state of the ions in the host crystal produces changes in the valence state of a controlled number of host ions. Such controlled valency systems show interesting semiconducting properties. A good example of a controlled valency semiconductor is NiO doped with Li_2O where the number of Ni^{3+} ions in the

a

b
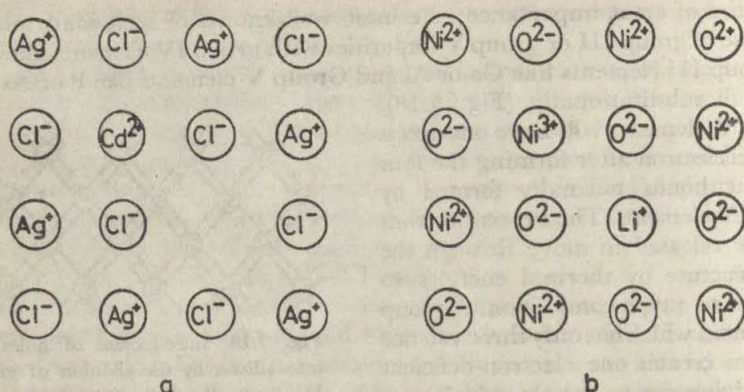
Fig. 7.19 (a) Introduction of a cation vacancy in AgCl by substitution of Ag⁺ by Cd²⁺. (b) Effect of addition of monovalent Li impurity on NO.

system is determined by the number of Li^+ ions (Fig. 7.19b). The composition of the resulting material may be written as $Ni^{3+}_{1-2y} Ni^{2+}_y Li^+_y O$. With 10 atom per cent of Li, this material is black in color and exhibits high electrical conductivity (p type); NiO is pale green in colour and is an insulator.

The most important criterion in the defect chemistry of ionic crystals is the principle of electroneutrality or charge compensation. The creation of vacancies or new valence states of ions in crystals by the addition of impurities is determined by this simple principle (see Figs. 7.17 and 7.19).

Line defects: Although the concept of dislocations was first introduced primarily to explain deformation in metals, it is now established that dislocations play an important role in crystal growth, crystal transformations, electrical conductivity and other solid state phenomena. Dislocations in crystals have been observed directly with the aid of electron microscopes.

Edge dislocations where an extra half-plane of atoms is inserted into the lattice are illustrated in Fig. 7.20. The dislocation consists of a line of atoms each of which is short of one coordinating atom than prescribed by the crystal structure. The dislocation extends along a direction perpendicular to the plane of the paper and is designated by the symbol T. It can be seen from Fig. 7.20
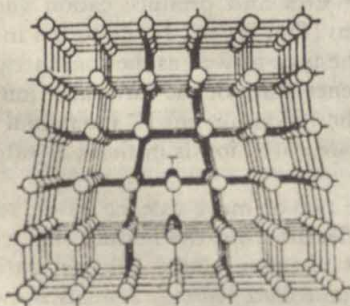
Fig. 7.20 Edge dislocation   Fig. 7.21 Screw dislocation
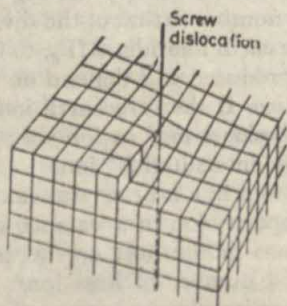
that the dislocation line marks the edge of the plane of atoms inserted part-way into the crystal. Edge dislocations are also called Taylor dislocations or Taylor–Orowan dislocations.

Another kind of dislocation called the *screw dislocation* described by Burgers (also known as Burgers dislocation) consists of a line of atoms with distorted coordination polyhedra. This is caused by a displacement of atoms in one part of the crystal with respect to the rest of the crystal, the displacement direction being parallel to the dislocation line; as shown in Fig. 7.21, the row of atoms marks the termination of the displacement in the dislocation. The polyhedron is not regular in the disturbed region and the distortion decreases progressively with increasing distance from the dislocation line.

An edge dislocation can be produced by applying a shear to the crystal and the net displacement of atoms in one part of the crystal relative to the atoms in the other part of the crystal determines the magnitude of the dislocation. Since atoms in a crystal occupy equilibrium positions, the net displacement is always equal to one of the equilibrium distances between atoms. If this distance (*Burgers vector*) is equal to the unit lattice translation, the dislocation is referred to as a unit dislocation. If the Burgers vector is shorter than a unit translation, the dislocation is called a partial dislocation.

Plane defects: Many of the solid state materials are polycrystalline in nature. Polycrystalline solids consist of a number of small randomly oriented interlocking crystals (*grains*). The *grain boundary* generally has a complex structure which in some way conforms to the shapes and orientations of the adjacent grains. Since a grain boundary forms a discontinuity in the periodicity of the lattice, it may be considered to be another kind of imperfection. The disturbed region in the boundary layer may consist of a few atom layers and acts as a bridge between the two neighbouring mismatched crystalline regions. The angles between the adjacent grains are generally large due to random orientation of the initial grains. Since grain boundaries may contain a number of imperfections like impurities, interstitials, etc. (expelled by the grains during their growth), it often becomes difficult to understand the electrical, mechanical and other properties of polycrystalline solids.

Another important kind of plane defect found in crystals arises from *stacking faults*. In the cubic close-packed structures, we have the sequence ...*ABCABC*... while in the hexagonal case we have the sequence ...*ABAB*.. (see section 7.4.1). A fault in a stacking sequence as in *ABABABCBABA* or *ABCABCBCABCABC*, occurs when the packing is cubic instead of hexagonal or vice versa. The sequence in the planes before and after the stacking fault would, however, be normal.

7.7 PROPERTIES OF SOLIDS

There is a close relationship between the physical properties of a solid and its structure and chemical composition. We shall now examine a few of the important properties of solids to illustrate the wide variety of possibilities. Some of these properties are exploited for various new innovations in electronic and magnetic devices such as transistors, computers, telephones, etc. The information explosion in inorganic and organic solid state materials has been so great in recent years that it would be impossible to list representative examples of all classes of materials in an elementary chemistry text of this sort.

7.7.1 Electrical Properties

Based on their electrical conductivity, solids can be broadly classified into three types: metals, insulators and semiconductors. Conductivity of solids varies anywhere from 10^8 ohm^{-1} cm^{-1} in metals to 10^{-22} ohm^{-1} cm^{-1} in insulators. Electrical conductivity of solids may arise through the motion of electrons and holes (electronic conductivity) or other charged imperfections and ions (ionic conductivity). Substances like pure alkali halides where the conduction is only through ions, are generally insulators since the mobilities of ions are very much lower than those of holes or electrons. However, presence of vacancies or other imperfections could markedly increase the conductivity of ionic solids. Conductivity of metals generally decreases with increase in temperature while that of semiconductors increases with temperature.

At laboratory temperatures, conductivity of *metals* is nearly independent of impurities and lattice defects. The electron concentration is mainly determined by the nature of the metal (number of valence electrons in the metal) and the mobility by the lattice vibrations. At low temperatures, however, lattice vibrations are quite insignificant and the conductivity should be infinite. However, this is not true because of the presence of lattice imperfections and impurities. It is thus convenient to use the resistance ratio $\rho_{300K}/\rho_{4\cdot2K}$ as a measure of purity of the metal.

Unlike metals, the conductivity of *semiconductors* and *insulators* is mainly determined by the impurities and defects. Electrons and holes produced by the ionisation of defects contribute to the electronic conduction in these solids. The behaviour of insulators and semiconductors can be explained in terms of the band model. If the band structure of an element is such that the fully occupied band is separated by a large energy gap from the vacant band, then conduction is not possible. This situation is found in good insulators like diamond or MgO. On the other hand, if the energy gap is small, promotion of electrons can take place by raising the temperature—the higher the temperature greater is the number of electrons promoted and greater is the conductivity. This is the characteristic behaviour of semiconductors (e.g. SnO_2, $SrTiO_3$). Fig. 7.22 shows the schematic band structures of metals, insulators and semiconductors.

When the thermally produced electrons and holes are mainly responsible for the conductivity of a semiconductor (generally at higher temperatures) rather than the electrons and holes produced by donors and acceptors (as in

Empty conduction band — Forbidden energy gap — Filled valence band

(a) Insulator   (b) Metal   (c) Intrinsic semiconductor
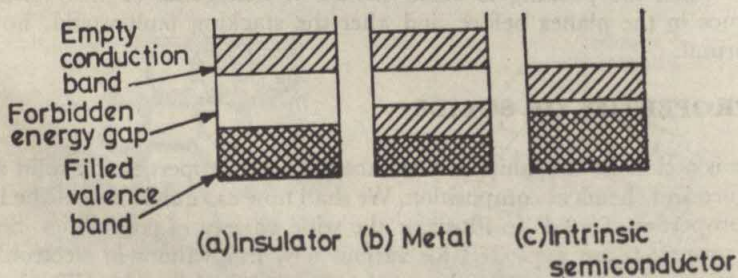
Fig. 7.22 Schematic band structures of metals, insulators and semiconductors

doped Ge or Si), the region is called the intrinsic region. At lower temperatures where the conductivity is mainly determined by the concentration of donors and acceptors, the region is called extrinsic. We should recapitulate here that pure germanium or silicon by itself would be an insulator; only by doping with a group III or V impurity can we increase the conductivity at ordinary temperatures (see section 7.6).

In Table 7.7, we have summarised the electrical properties of some oxides of transition metals to illustrate the wide variations found in such materials; a similar variety is also exhibited by sulphides and other chalcogenides. It is particularly interesting that the monoxides, all of which possess the NaCl structure, show such marked differences in electrical properties; some are metallic while others are semiconductors or insulators. The oxide, ReO_3 is comparable to copper in its conductivity. Oxides like TiO and NbO become *superconductors* at low temperatures (≈ 2 K). There are many oxide systems like the *tungsten bronzes*, $M_x WO_3$ (M = alkali or some other metals and x = variable concentration) and *perovskites* like $LaTiO_3$ and $LaNiO_3$ which exhibit metallic conductivities.

Table 7.7 Electrical Properties of Typical Transition Metal Oxides

TiO(M)	VO(M)	CrO(?)	MnO(I)	FeO(S)	CoO(S)	NiO(S)	CuO(S)
Ti$_2$O$_3$(M–S)	V$_2$O$_3$(M–S)	Cr$_2$O$_3$(S)	Mn$_2$O$_3$(S)	Fe$_2$O$_3$(S)			Cu$_2$O(S)
TiO$_2$(S)	VO$_2$(M–S)	CrO$_2$(M)	MnO$_2$(D)		Co$_3$O$_4$(S)		
	V$_2$O$_5$(S)		Mn$_3$O$_4$(S)	Fe$_3$O$_4$(D)			

M=metal; I=insulator; S=semiconductor; M–S=shows a transition from metal to semiconductor behaviour at a certain temperature; ?=substance not known; D=degenerate semiconductor (high conductivity with little or no variation with temperature)

In addition to electronic semiconductors where the band picture is applicable, there are many materials where the semiconduction is due to the hopping of electrons from one site to another (see section 7.6.1). Examples of these are oxides where cations of more than one valence state are present as in Pr_6O_{11}, NiO doped with LiO, etc.

Ionic conduction in a solid involves migration of atoms, ions or other charged species under applied field. This ion migration becomes possible because of the presence of vacancies or/and interstitials in the ionic solids. Conductivity measurements in ionic solids like NaCl give valuable information on the energy required for the creation of defects, as well as their migration energies.

7.7.2 Magnetic Properties

Materials can be divided into different classes depending on their response to magnetic fields (see section 3.12). *Diamagnetic* materials (like NaCl or ZrO_2) are weakly repelled by magnetic fields. In *paramagnetic* materials there are permanant magnetic dipoles due to the presence of atoms, ions or molecules with unpaired electrons (e.g. O_2, NO, Na atoms, Ti_2O_3, VO_2) and these materials are attracted by magnetic fields; they, however, lose their magnetism in the absence of a magnetic field. Solids like TiO_2 which should be diamagnetic often exhibit paramagnetism due to the presence of slight non-stoichiometry.

Unlike paramagnetic materials, *ferromagnetic* materials show permanent magnetism even after the magnetic field is removed (e.g. Fe, $Cu_2Mn\cdot Sn$, EuO, CrO_2). The explanation for the large magnetisation in these materials is that there are *domains* of magnetisation (consisting of about a million atoms or ions), all of which cooperatively direct their magnetic moments (spins) in the same direction. Once such a material is magnetised (with all domains oriented), it remains permanently that way. Iron, cobalt and nickel are the only three elements which show ferromagnetism at room temperature. Manganese has most of the properties required for ferromagnetism, but the metal atoms are too close; however, addition of copper to manganese enhances the spacing of atoms and the alloy is ferromagnetic.

We just mentioned that a spontaneous alignment of magnetic moments in the same direction gives rise to ferromagnetism. If the alignment of moments is in a compensatory way so as to give zero net moment, then we get *antiferromagnetism* in the material (e.g. MnO). *Ferrimagnetism* is found when the moments are aligned in parallel and antiparallel directions in unequal numbers resulting in a net moment (e.g. Fe_3O_4; ferrites of the formula $M^{2+}Fe_2O_4$, M = Mg, Cu, Zn, etc.). In Fig. 7.23, we have schematically shown the alignments

(a) ↑↑↑↑↑↑↑↑↑↑↑↑↑↑

(b) ↑↓↑↓↑↓↑↓↑↓↑↓↑↓

(c) ↑↑↓↑↓↑↓↑↑↓↑↓↑↓
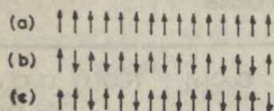
Fig. 7.23 Schematic alignments of magnetic moments in (a) ferromagnet, (b) antiferromagnet, and (c) ferrimagnet

Chemical unit cell

○ Fe^{+3} and Fe^{+2} (octahedral)
◔ Fe^{+3} (tetrahedral)

b
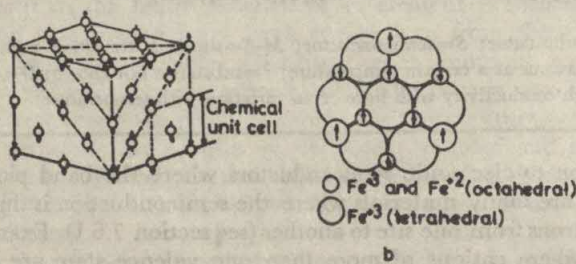
Fig. 7.24 Spin alignments in (a) MnO and (b) Fe_3O_4. In MnO, the unit cell dimension is doubled due to the presence of antiferromagnetism. In Fe_3O_4, Fe^{3+} ions in tetrahedral and octahedral voids have antiparallel spins. The net magnetisation is due to Fe^{3+} ions in octahedral voids.

of magnetic moments in ferro-, antiferro- and ferri-magnets. In Fig. 7.24 we have shown the spin alignments in antiferromagnetic MnO and ferrimagnetic Fe_3O_4. All these magnetically ordered solids transform to the paramagnetic state at a higher temperature due to the randomisation of spins. For example, V_2O_3 and NiO transform from the antiferromagnetic phase to the paramagnetic phase at 150 K and 523 K respectively. Ferromagnetic CrO_2 becomes paramagnetic at 395 K; a similar transition in ferrimagnetic Fe_3O_4 is at 850 K. Magnetic properties of some transitional metal oxides are shown in Table 7.8 to indicate the diversity.

Table 7.8 Magnetic Properties of Typical Transition Metal Oxides

$TiO(p)$	$VO(p)$	$CrO(?)$	$MnO(af)$	$FeO(af)$	$CoO(af)$	$NiO(af)$	$CuO(p)$
$Ti_2O_3(p)$	$V_2O_3(af)$	$Cr_2O_3(af)$	$Mn_2O_3(af)$	$Fe_3O_4(afw)$	$Co_3O_4(af)$		$Cu_2O(d)$
$TiO_2(d)$	$VO_2(p)$	$CrO_2(f)$	$MnO_2(af)$	$Fe_3O_4(fe)$			
	$V_2O_5(d)$		$Mn_3O_4(fe)$				

p=paramagnetic; $?$=substance not known; af=antiferromagnetic; afw=antiferromagnetic with parasitic ferromagnetism; fe=ferrimagnetic; f=ferromganetic

7.7.3 Dielectric Properties

In insulators, electrons are closely bound to individual atoms or ions and they do not generally migrate under an applied electric field. However, dipoles are created by a shift in the charges resulting in polarisation. (i) These dipoles may align themselves in an ordered manner such that there is net dipole moment in the crystals or (ii) they may align themselves in such a manner that the dipole moments cancel each other. (iii) It is also possible that there are no polar species (dipoles) in the crystal, but only ions are present. Crystals where situation (i) is found, exhibit *piezoelectricity*. When such a crystal is deformed by mechanical stress, electricity is produced due to the asymmetric displacement of ions or conversely if an electric field is applied to the crystal, there will be atomic displacements causing mechanical strain. Thus, a piezoelectric crystal acts as a mechanical $\rightleftharpoons$ electrical transducer. Some of the polar crystals, when heated, produce a small electric current or *pyroelectricity* due to the asymmetric variation in interatomic distances.

In some of the piezoelectric crystals, the dipoles are permanantly lined up (spontaneously polarised) even in the absence of an electric field and the direction of polarisation can be changed by applying an electric field. This phenomenon is called *ferroelectricity* by analogy with ferromagnetism. Barium titanate ($BaTiO_3$), sodium-potassium tartrate (Rochelle salt), sodium nitrate ($NaNO_3$) and potassium dihydrogen phosphate (KH_2PO_4) are typical ferroelectric solids. The occurrence of ferroelectricity undoubtedly depends on the structure and only certain geometric arrangements in the crystal can exhibit this phenomenon. If the dipoles in alternate polyhedra point up and down, there will be no net dipole moment and the crystal is said to be *antiferroelectric*. Lead zirconate ($PbZrO_3$) is a typical antiferroelectric. Both ferroelectric and antiferroelectric crystals transform at some temperature to the paraelectric phase where the dipoles are randomly oriented.*

7.8 RETROSPECTION

Properties of solids vary depending on the nature of bonding or cohesive forces present in them. Thus, in ionic solids the cohesive energy (lattice energy) mainly arises from coulomb attraction amongst ions. In metals, electrons are

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*Note the interesting similarity between ferro-, antiferro- and para-electricity and the corresponding phenomena in magnetism. In a *ferro*electric or a *ferro*magnetic substance, there is no need to have iron. The reason for this terminology is that iron was the first substance studied amongst ferromagnets. The similarity of the phenomenon of spontaneous polarisation in ferroelectrics to the spontaneous magnetisation in ferromagnetic materials is responsible for the name given to the former.

essentially free to move and we can describe metals in terms of electron bands formed by molecular orbitals. Crystals can possess various structures which can be studied by x-ray diffraction and the structures can be classified in terms of fourteen types of lattices. Structures of metals as well as of simple ionic compounds can be understood in relation to closest-packed structures formed by special atoms or ions. Relative sizes of the atoms and ions determine the sizes of voids in the structure and, therefore, the coordination of ions in ionic solids. An understanding of crystal structure and chemistry is valuable in understanding properties of substances and we shall point out some of these aspects wherever necessary in our discussion of descriptive inorganic chemistry.

Deviations from the perfectly ordered arrangement are found in real crystals and these imperfections can be intrinsic or extrinsic. Electrons in solids can be treated as defects. Besides electronic imperfections, we have a whole variety of atomic imperfections. Defects in solids cause interesting changes in properties. Solids exhibit a wide variety of electrical, magnetic and other properties and these are exploited for various devices in the modern world.

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PROBLEMS

7.1   A metal M forms a crystalline chloride of the formula MCl. The sublimation energy of M is 30 kcal/mol and the formation energy of MCl from the elements is -130 kcal/mol. Ionisation energy of M is 160 kcal/mol.   Calculate the lattice energy of MCl.

7.2   KCl and RbCl have the same structure as NaCl. Calculate the electrostatic energy in these crystals making use of the ionic radii given in the text.

7.3   Draw the unit cells of copper (FCC) and NaCl and compare the two with respect to the coordinates and coordination numbers of atoms (or ions).

7.4   What is the simplst formula of a solid containing atoms A and B if A atoms occupy the corners and B atoms occupy the face-centres of a cubic unit cell?

7.5   The density of crystalline NaCl is 2·165 g/cc. What is the length of the cube edge of NaCl? What would be the dimensions of a cube containing one mole of NaCl?

7.6   When a crystal of a substance was examined by x-rays (0·59 A wavelength) the first Bragg diffraction was seen at $\theta = 10°$. Calculate the separation of the planes involved.

7.7   A metal has a face-centered cubic (CCP) structure with a cube edge of 4A. What is the size of the largest atom that can fit in the interstices of the lattice of this metal?

7.8   Iron occurs in BCC as well as FCC structure. If the effective radius of iron atom is 1·24A, calculate the density of iron in both these structures.

7.9   A simple cubic lattice consists of eight spheres of radius R in contact. What is the volume of the cube that encloses these eight cubes? What will be the fraction of the volume that is free?

7.10 The face-centered unit cell of nickel has a cube edge of 3·5239A. The density of nickel is 8·9 g/cc. Compute the Avogadro number from these data.

7.11 Show that the critical radius ratio of 0·225 gives tetrahedral coordination.

7.12 What is the coordination number of Mn in MnO if $r_{Mn} = 0·80A$ and $r_O = 1·40A$?

7.13 How does the density of a solid get affected by Schottky defects and Frenkel defects?

7.14 An oxide of the formula TiO has the NaCl structure with a cube edge of 4·18A. The pyknometric density of the oxide is 4·92 g/cc. Calculate the per cent occupancy of Ti and O sites in the solid.

7.15 A small number of K^+ ions in KCl are substituted by Pr^{3+} ions. Draw the possible structures of the defect solid.

7.16 The ratio of Fe^{3+} to Fe^{2+} in a non-stoichiometric sample of FeO is 0·1. What fraction of the cation sites is occupied by vacancies? By what factor is the density changed (assuming no change in lattice constant)?

7.17 Co_3O_4 is ferrimagnetic. Draw a figure showing the orientation of spins indicating the distribution of cobalt ions in tetrahedral and octahedral voids.

7.18 A solid is a semiconductor at ordinary temperatures and pressures. Can you possibly transform it into a metal? How? Explain your answer briefly.

7.19 A perfect ionic crystal like NaCl should be an insulator. Still we find that NaCl conducts electricity appreciably at fairly high temperatures. Why? Will divalent cation impurities affect the conductivity?

7.20 Write briefly some of the important applications of the following materials: (i) semi-conductor grade germanium and silicon, (ii) ferrites, (iii) ferroelectric materials, (iv) GaAs, and (v) chalcogenides of zinc and cadmium.

8

The Liquid State
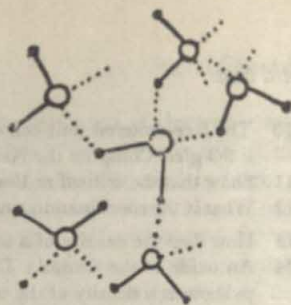
If I were in the world of molecules, I would rather be in liquid state with some freedom of gases and some order of solids.

<div align="right">ANON</div>

Water existed on earth long before life began and is fundamental to most life processes. Although simple in structure, the ubiquitous water molecule is one of the most complex substances known; a complete understanding of its intermolecular behaviour still eludes us.

<div align="right">FELIX FRANKS</div>

Almost all the chemical processes which occur in nature, whether in animal or vegetable organisms, or in the non-living surface of the earth, . . ., take place between substances in solution.

<div align="right">W. OSTWALD</div>

We have already seen that the main characteristics of the gaseous state are random translational motions of molecules and relatively little intermolecular interaction. In the solid (crystalline) state, on the other hand, the individual atoms or molecules are fixed in position in an ordered arrangement and there is no translational motion. Both these states by virtue of their relatively simple behaviour can be described satisfactorily in terms of theoretical models. Liquids are, however, more complex to understand since there is neither completely random motion nor a completely ordered arrangement of atoms or molecules; this state lies between the gaseous and crystalline states. There exists more disorder in liquids compared to solids since we need to supply thermal energy to melt solids (or since melting of solids is an endothermic process); the kinetic energies of molecules in liquid state are also appreciable.

In Fig. 8.1 we have shown two-dimensional schematic representations of the three states of matter. The gas is dilute and disordered. A common feature to both liquids and solids is the closeness of packing of molecules. Most solids expand when they melt by about 5–15 percent in volume* (or by about 3–4 per cent in molecular spacing) and the molecular arrangements in the two states differ significantly. In a perfect crystalline solid, the ordered arrangement

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*There are a few exceptions like water and bismuth which contract on melting.
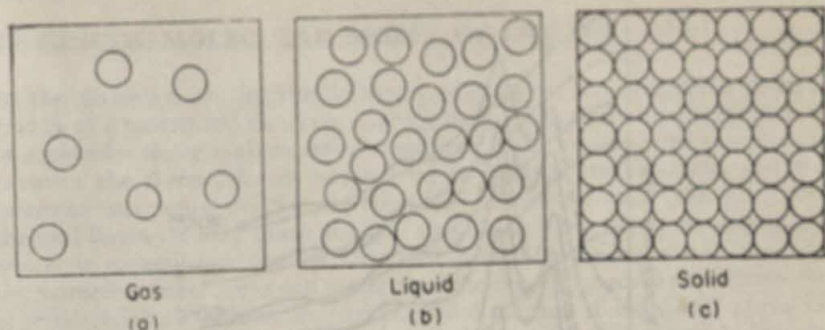
Fig. 8.1 Schematic representation of the states of matter

extends right up to the surface and crystalline solids are, therefore, said to exhibit long-range order. In liquids the well-ordered arrangement extends over a short-range only, say five or six molecular diameters. This view is supported by studies of the diffraction of x-rays by liquids.

8.1 STRUCTURE OF LIQUIDS

Fig. 8.2 shows the x-ray diffraction patterns of liquid mercury compared with those of crystalline mercury. We may recall that the sharpness of the diffraction lines reflects the extent of long-range order in crystals; the x-ray patterns of very fine powders are, therefore, very diffuse. We see from Fig. 8.2 that in contrast to crystalline mercury (which exhibits sharp diffraction lines), the liquid mercury shows only a few broad maxima or minima which become broader and more diffuse as the temperature is raised. The presence of these maxima and minima suggests that liquids possess some orderly arrangement, although the fewer number of maxima indicate the presence of only short-range order.

X-ray diffraction data on liquids are interpreted by computing the *radial distribution function** from the diffraction pattern. This function gives the probability of finding other atoms at various distances from a certain atom. Fig. 8.3 shows the plot of the radial distribution function $4\pi r^2 \rho$ as a function of r; here ρ is the number of atoms per centimetre at a distance r. The area under the curve between two values of r gives the number of atoms contained in the corresponding spherical shells and from this, one can estimate the coordination number in liquid (this is the average number of atoms surrounding a central atom or in other words the number of nearest neighbours). Such studies reveal that atoms in liquid mercury exist in an environment that is nearly close-packed. Short-range order calls for about twelve nearest neighbours, but random movements loosen the close packing.

We must point out here that the x-ray diffraction pattern of a liquid is not the consequence of any definite arrangement of the atoms (or molecules) but instead it represents a time average over all the positions of the atoms resulting from their translational motion.

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*This type of function was introduced in Chapter 3 to describe the electron motion in a hydrogen atom.
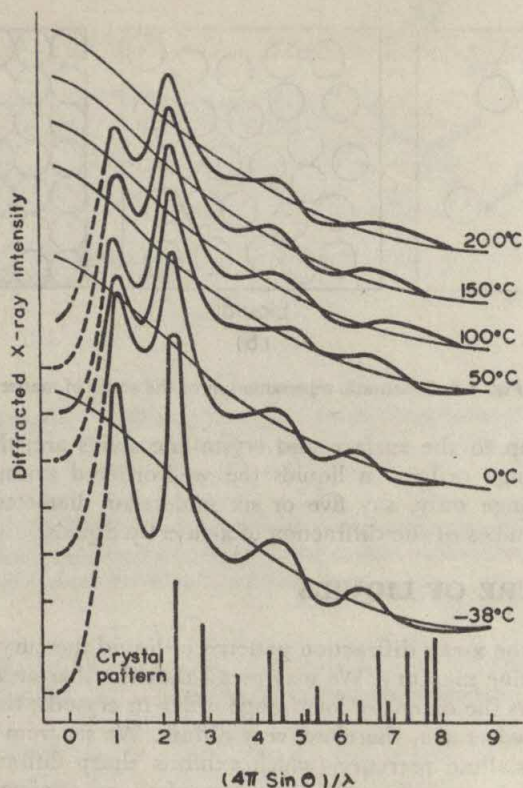
Fig. 8.2 Intensity of x-rays diffracted by liquid mercury versus angular function $4\pi \sin \theta/\lambda$. Note the diffused nature of the diffraction obtained from liquid mercury as contrasted with the sharp lines from crystals. Smooth curves would be obtained if there is no structure.
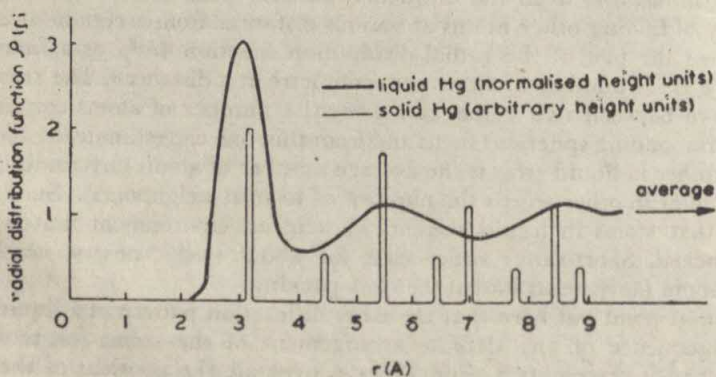
Fig. 8.3 Radial distribution function plotted against radius measured from an arbitrary atom chosen as the origin for liquid mercury and solid mercury. Note that with the liquid, the structure is lost beyond distances of 10 A; with the solid it persists indefinitely.

8.2 KINETIC MOLECULAR MODEL OF LIQUIDS

In the discussion on the kinetic theory of gases we found that the thermal energy of a monatomic molecule is given by $3kT/2$ and that the arrangement of molecules under a given set of conditions is the result of the competition between the thermal forces which tend to disorder the molecules and the intermolecular attractive forces which tend to order them. With gases, the thermal forces are very much stronger than the intermolecular forces and the atoms or molecules in gaseous state have a random arrangement. In solids, the attractive forces are much larger than the thermal forces and we have the ordered structure without any translational motion of individual atoms or molecules. In liquids, the attractive forces are sufficiently strong to lead to a condensed state but not strong enough to entirely eliminate the translational energy of the atoms or molecules. Thus in terms of the kinetic theory model, the nature of liquid state is described as follows: (*i*) There are appreciable attractive forces between the molecules. (*ii*) The molecules are relatively close together. (*iii*) The molecules are in constant, random motion. (*iv*) The average kinetic energy of molecules in a given sample is proportional to the absolute temperature.

Now we shall explain some of the observed macroscopic properties of the liquids on the basis of this model.

Volume: Liquids, unlike gases, have a definite volume. They maintain their volume whatever be the shape or size of the container. A 25 ml sample of a liquid occupies a volume of only 25 ml whether it is placed in a beaker, a conical flask or a large round-bottomed flask. It remains confined to the lower part of the vessel whereas a gas spreads out to fill the whole volume available to it. Gases do not maintain their volume because the molecules in a gas are relatively independent of one another and can move rather freely into any available space. In liquids, however, the molecules are close together so that the mutual attractions are strong and hence they are not quite free to occupy any space.

Density: The closer approach of molecules in the liquid state, as opposed to the gaseous state, also provides an explanation for the fact that densities of liquids are about thousand times greater than the densities of gases under comparable conditions. Compare, for example, the density of water at 100°C and 1 atm (0·958 g/ml) with that of water vapour at the same temperature and pressure, as calculated from the ideal gas law ($\rho = PM/RT = 0 \cdot 000588$ g/ml).

Compressibility: Liquids are much less compressible than gases. This may be accounted for by the very small free space available in liquids. At 25°C, an increase in pressure from 1 atm to 2 atm decreases the volume of a sample of liquid water by only 0·0045 per cent. The same change in pressure decreases the volume of an ideal gas by 50 per cent. In liquids, molecules are very much closer to one another (compared to in gases) and are, therefore, virtually incompressible.

Diffusion: Like gases, liquids also diffuse but they do so rather slowly.*
Since diffusion involves movement of molecules from one position to another,
in the liquid state molecules will undergo a number of collisions with the neigh-
bouring molecules even as they move through a small distance. In gases,
however, there is less obstruction to the moving molecules because of the large
empty space available for movement.

8.3 VAPOUR PRESSURE

We know that when a liquid is placed in an open vessel it gradually dis-
appears because the liquid is converted into its vapour. This process is known
as evaporation. How does evaporation occur? Molecules in the liquid phase
escape from the surface of the liquid into the space above the liquid.   This
happens in spite of the strong attractive forces between the molecules in a liquid.
To understand how molecules are able to escape from a liquid, remember that
the molecules in a liquid are in constant motion and possess kinetic energy.
Although the temperature of the liquid is uniform and the average kinetic
energy of the molecules is constant, not all the molecules have the same kine-
tic energy. In liquids, as in gases, molecules have a distribution of kinetic ener-
gies ranging from very low values to very high values. Consequently, a certain
fraction of the molecules at the surface will have such large kinetic energies
as to overcome the attractive forces of the neighbours and to escape into the
space above the liquid surface. If the temperature is kept constant, the remain-
ing liquid will have the same distribution of molecular energies and the most
energetic fraction will continue to escape from the liquid into the vapour
state. If the liquid is in an open vessel, evaporation will continue until ulti-
mately no liquid remains.

The number of molecules escaping from the surface depends upon the inter-
molecular attractive forces. When these forces are stronger fewer molecules
escape. The ability to evaporate, or the volatility of a liquid, indicates the
strength of intermolecular forces in the liquid. Ether evaporates more readily
than alcohol and alcohol evaporates quicker than water. The intermolecular
attractive forces vary in the order, ether < alcohol < water. A rise in temperature
increases the kinetic energy of molecules and they can escape more readily
from the liquid surface. Hence evaporation of liquids increases with rise in
temperature.

Since evaporation is a surface phenomenon, the increase in surface area increases the rate of
evaporation. For example, a 5 ml sample of ether placed in a beaker evaporates faster than the
5 ml sample of ether placed in a test tube. That is why wet clothes are spread out for drying them
quicker. Large surface area affords greater opportunity for the molecules of a liquid to escape.
We have learnt that during evaporation, molecules having higher energy escape from the surface.
They carry with them more than the average amount of kinetic energy and the less energetic
molecules remain behind. This is why we find in our common experience that temperature
(which is proportional to kinetic energy) falls when liquids evaporate. For example, a drop of
ether or chloroform produces cool sensation on the skin due to evaporation.

*When a few drops of ink are carefully released in water, there is a sharp boundary between
the ink cloud and water. After some time the colour spreads throughout the water. The time
taken for this to happen is appreciable. But when a drop of bromine is placed at the bottom
of a container it becomes vapour which soon spreads throughout the container. In gaseous
state the diffusion is very rapid.

The quantity of heat required to evaporate a given liquid at constant temperature is defined as the *heat of evaporation* or *heat of vapourisation* (also see Chapters 9 and 10). The quantity of heat depends on the strength of forces of attraction between the molecules in a liquid. Water has relatively high heat of vapourisation (Table 8.1) because of the presence of strong attractive forces. When one mole of water is completely vapourised at 25°C, it absorbs 10,519 cal from its surroundings:

$$H_2O \ (l) + 10,519 \ cal \rightarrow H_2O \ (g)$$
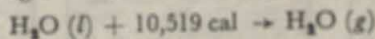
Table 8.1 Physical Properties of Liquids Related to Intermolecular Forces

Liquid	Normal BP (K)	Critical Temperature (K)	Vapour pressure at 20°C mm Hg	Heat of vapourisation kcal/mol (at the boiling point)[1]
Mercury	630·0	1750·0	0·0012	14·20
Water	373·0	647·0	17·5	9·70
Benzene	353·0	562·0	75·0	7·30
Methyl alcohol	337·9	513·0	—	8·42
Ether	308·0	467·0	442·0	6·20
Ethane	184·0	305·0	27000·0	3·50
Oxygen	90·0	154·0	—	1·60
Helium	4·2	5·2	—	0·08

[1]The heat of vapourisation of a liquid varies to some extent with temperature. For example, for water it is 10·519 kcal/mol at 25°C and 9·7 kcal/mol at the boiling point (100°C).

It was mentioned earlier that a liquid placed in an open vessel evaporates completely. If, however, the liquid is allowed to evaporate in a closed system such as a stoppered bottle, evaporation starts and after some time, the level of the liquid does not change further and remains constant. This may be explained as follows: Molecules which evaporate from the liquid surface are confined to a limited space. These molecules may collide among themselves or with the molecules of air and in that process are pushed back to the surface of the liquid, a process referred to as condensation. At the start, the rate of evaporation is much greater than the rate of condensation. But as the molecules accumulate in the space above the liquid, the rate of condensation progressively increases. Eventually, a condition is reached when the rate of condensation becomes equal to the rate of evaporation. When two opposing processes proceed at exactly the same rate, the system is said to be in a state of *dynamic equilibrium* (Fig. 8.4). Although in such a state, the system is not in a state of rest, there is no observable change in the system. The amount of the liquid in the bottle remains constant. The number of molecules in the vapour above the liquid is also constant (since on average, for every molecule that evaporates there is another which condenses). The molecules in the vapour phase exert pressure. This pressure is known as *equilibrium vapour pressure* or simply vapour pressure. The vapour pressure of a liquid has a characteristic value at a given temperature.
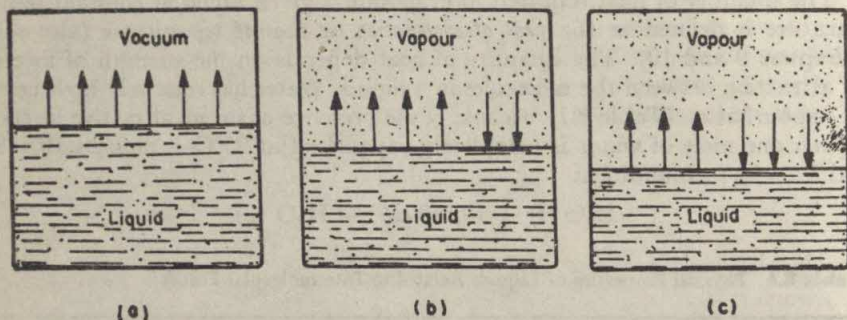
Fig. 8.4 Attainment of equilibrium in the evaporation of a liquid: (*a*) initial state, with evacuated space above liquid, (*b*) intermediate state, and (*c*) equilibrium state

Measurement of vapour pressure: A simple apparatus for determining vapour pressure of liquids consists of a glass bulb provided with a stop cock and a manometer (Fig. 8.5). The liquid is placed in the bulb and all the air and other foreign molecules are pumped out by means of a suction pump.* The stop cock *S* is closed. The liquid evaporates and the pressure
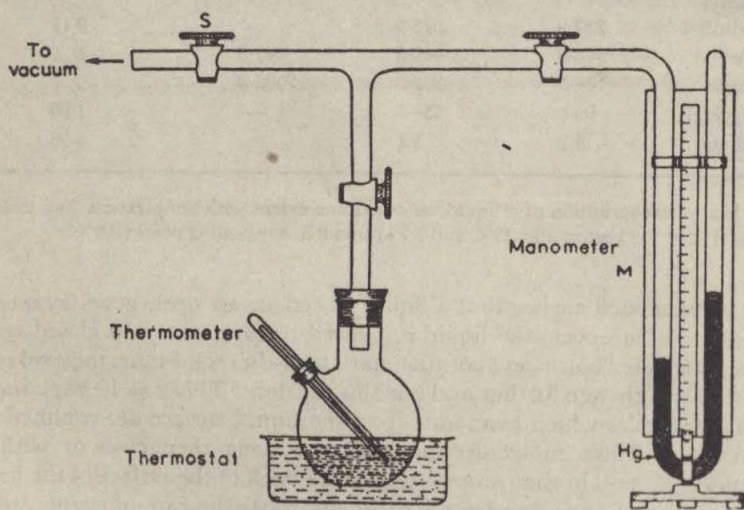
Fig. 8.5 Measurement of vapour pressure

caused by the molecules in the space above the liquid is measured with manometer, *M*, after the equilibrium is reached. For measuring vapour pressure at different temperatures, the bulb may be immersed in a thermostat and the temperature varied. Remember that the magnitude of the equilibrium vapour pressure depends upon the nature of liquid, and the temperature of the liquid.

*To pump out all the air and other foreign molecules, the liquid is frozen and then the space above the liquid is evacuated. The frozen liquid is allowed to melt so that the dissolved air can escape; the liquid is refrozen and the air is evacuated again. This is repeated several times so that the space above the frozen liquid is a partial vacuum.
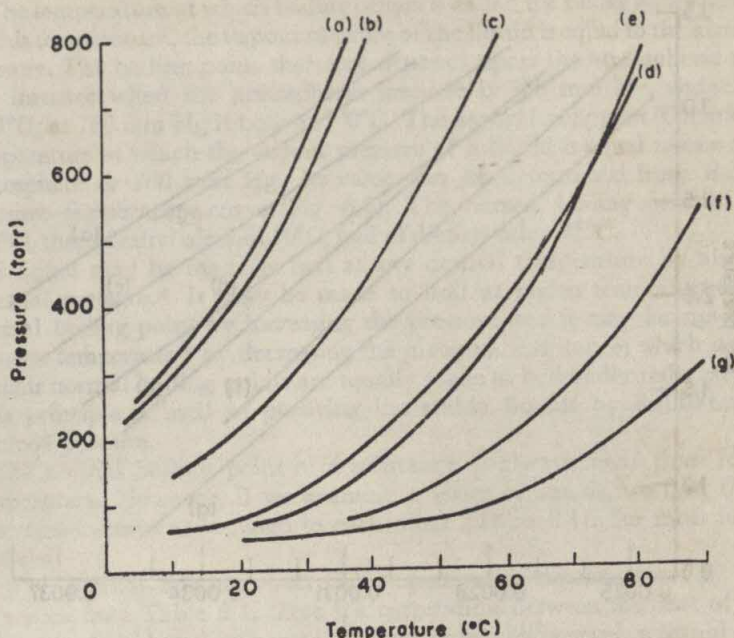
Fig. 8.6 Temperature dependence of vapour pressure of liquids: (*a*) Diethyl ether, (*b*) ethyl bromide, (*c*) acetone, (*d*) benzene, (*e*) ethyl alcohol, (*f*) water, and (*g*) octane

Vapour pressure and temperature: As indicated earlier the number of molecules escaping from the surface of the liquid increases with temperature resulting in an increase in the vapour pressure. Fig. 8.6 shows the temperature dependence of vapour pressure of some liquids.

Another way of showing these variations is illustrated in Fig. 8.7, where the logarithm of the vapour pressure is plotted against the reciprocal of the absolute temperature, T. This straight line follows the equation

$$\log P = -A\left(\frac{1}{T}\right) + B$$

where A and B are constants characteristic of the particular substance.

When a liquid is gradually heated, the temperature of the liquid rises and its vapour pressure increases. At lower temperatures the equilibrium vapour pressure is much less than the pressure of the atmosphere acting on the liquid surface, the vapour is therefore not able to push its way through the bulk of the liquid and only a small amount of vapour escapes into the air from the surface. If temperature is increased until the vapour pressure becomes equal to the atmospheric pressure, the vapour formed within the liquid can freely rise up through the liquid in the form of bubbles and escape into the air (Fig.8.8). When this happens, we say that the liquid is boiling.

Although boiling and evaporation are similar processes, they differ in some respects. While evaporation occurs spontaneously at all temperatures, boiling takes place only at a particular temperature at which the vapour pressure is equal to the prevailing pressure of the atmosphere. Vapourisation consists essentially of the diffusion of vapour molecules from the liquid into the

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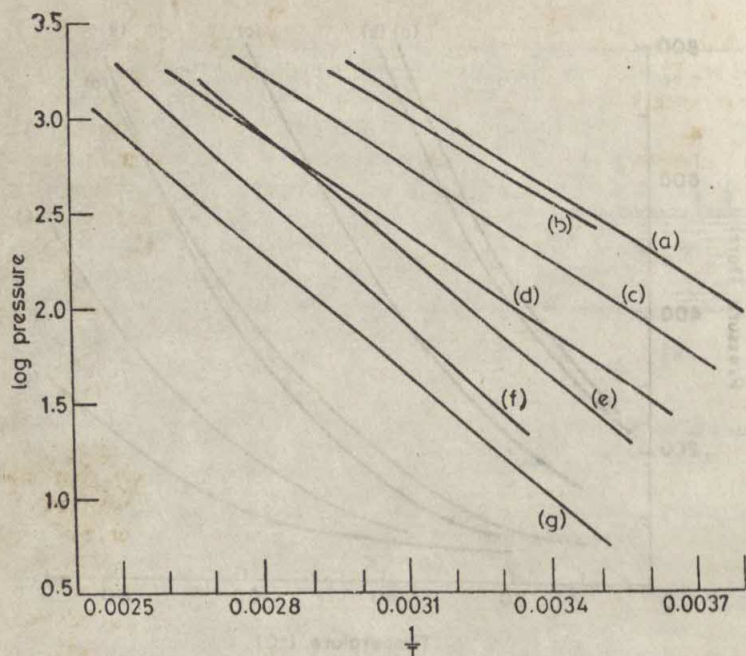
Fig. 8.7 Log P vs $1/T$ for the vapour pressure of several liquids: (a) Diethyl ether, (b) ethyl bromide, (c) acetone, (d) benzene, (e) ethyl alcohol (f) water, and (g) octane
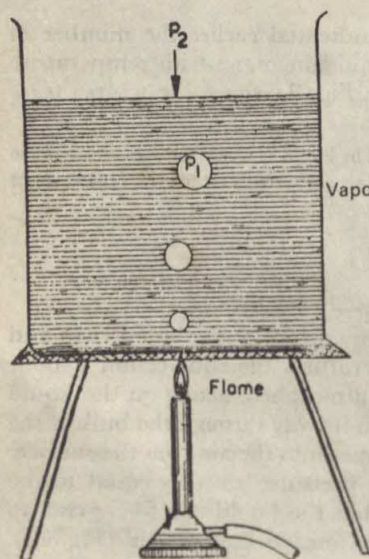
Fig. 8.8 Boiling of a liquid. At the boiling point of a liquid, vapour pressure of liquid P_1 is equal to pressure on liquid surface, P_2. (Actually for the vapour bubble to be formed within the liquid, the pressure within the bubble must be slightly greater than the total pressure at the point where the bubble is formed. The pressure at the point where the bubble is formed will, of course, be slightly greater than the pressure at the surface.)

atmosphere. Vapour from a boiling liquid however escapes with sufficient pressure to push back and displace any other gas present over the surface of the liquid rather than diffusing through it. Another point of difference between evaporation and boiling is that evaporation takes place only at the surface of the liquid whereas boiling involves the formation of bubbles of vapour below the surface of the liquid.

The temperature at which boiling occurs is called the *boiling point* of the liquid. At this temperature, the vapour pressure of the liquid is equal to the atmospheric pressure. The boiling point therefore depends upon the atmospheric pressure. For instance when the atmospheric pressure is 700 mm Hg, water boils at 97·7°C; at 760 mm Hg it boils at 100°C. The *normal boiling point* is defined as the temperature at which the vapour pressure of a liquid is equal to one standard atmosphere or 760 mm Hg. Its value can be determined from the vapour pressure–temperature curve (Fig. 8.6). The normal boiling point of water is 100°C, that of ethyl alcohol 76°C, and of diethyl ether 35°C.

A liquid may be made to boil at any desired temperature by altering the external pressure.* It may be made to boil at higher temperature than the normal boiling point by increasing the pressure and it may be made to boil at lower temperature by decreasing the pressure. Substances which decompose at their normal boiling points are usually made to boil under reduced pressure. This principle is used in purifying less stable liquids by distillation under reduced pressure.

The normal boiling point of a substance is always lower than its critical temperature. However, if we examine a series of liquids, we find that these two temperatures are related to each other (Table 8.1). For most liquids we find that

NORMAL BOILING POINT $(K) = \frac{2}{3}$ CRITICAL TEMPERATURE (K)

As we see from Table 8.1, there is a correlation between the heat of vapourisation of a liquid and its normal boiling point. In general, a liquid in which strong intermolecular forces contribute to its high heat of vapourisation, will also have a high boiling point, a high critical temperature and a low vapour pressure at room temperature.

8.4 SURFACE TENSION

In the preceding sections it has been mentioned that molecules in liquids attract one another. A molecule, A, which lies entirely inside the liquid is attracted equally on all sides (Fig. 8.9) and the net pull on the molecule is zero. The case of molecule B at the surface is, however, different. It is only partially surrounded by other molecules and there being no molecules above it, it is subjected only to attractive forces of molecules below it (see Fig. 8.9). Molecule, B, therefore, experiences a net downward attractive force that is perpendicular to the plane of the surface. This attractive force pulls as many molecules as possible from the surface to the interior of the liquid and tends to make the surface area of the liquid as small as possible. The surface of the liquid, therefore, contracts and exhibits a state of tension.

Surface tension of a liquid

Fig. 8.9 Forces on a molecule at the surface and interior of a liquid. Arrows show direction of attractive forces.

*Remember that there is an upper limit of temperature (critical temperature) to the existence of liquid phase (see Chapter 6). Above this temperature, substances will only remain in the gaseous state.

The surface tension of a liquid is defined as the work (energy) required to expand the surface of a liquid by unit area:

SURFACE TENSION = WORK TO INCREASE SURFACE BY UNIT AREA

$$= \frac{\text{WORK}}{\text{CHANGE IN AREA}} = \gamma$$

It is therefore expressed in ergs/cm^2 and denoted by the symbol γ. Since erg/cm^2=dynes cm/cm^2, γ can be thought of either as work (energy) per unit area or force per unit edge of surface. The values of γ for a few liquids are given in Table 8.2.

Table 8.2 Surface Tension (γ) of a few Liquids at 20°C (dynes/cm or ergs/cm^2)

Liquid	γ	Liquid	γ	Liquid	γ
Water	72·75	Benzene	28·9	Mercury	475
Alcohol	22·3	Toluene	28·3	Carbon tetrachloride	26·8
Diethyl ether	17·0	Acetone	23·7	Glycerine	65·2

As surface tension is due to intermolecular attractive forces, the magnitude of surface tension is a measure of the strength of intermolecular attractive
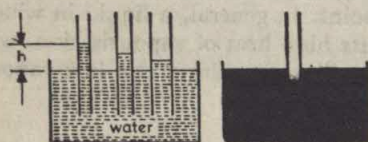
Fig. 8.10 Effects of surface tension: (left) If a liquid (like water) wets the walls of glass tube, then it rises to a height which is inversely proportional to the inner radius of the tube; (right) a liquid (like mercury) which does not wet glass, will be depressed in a capillary tube

forces. Surface tension causes a drop of liquid to assume a spherical shape because a sphere has a minimum surface area for a given volume of liquid. It is also responsible for the rise or fall of liquids in capillary tubes (Fig. 8.10).

Water has a natural tendency to be attracted to the surface of glass. The attraction between water and glass causes the water to spread into a concave film on the surface of the glass, thus increasing the surface area of water in a capillary tube. In order to reduce its total surface area, the liquid rises in the tube. The greater the surface tension of the liquid, the higher is its capillary rise. Consequently we can use capillary rise as a measure of the surface tension of a liquid. Molecules of mercury, however, are more strongly attracted to one another than they are to glass and mercury has very little contact area with glass. Consequently, mercury level in a capillary falls (Fig. 8.10).

Since the intermolecular attractive forces (which are responsible for surface tension) are comparatively smaller at higher temperature (Table 8.2), surface tension decreases with rise in temperature and this decrease continues up to the critical temperature of the liquid.

Surface tension is affected when substances are dissolved in a liquid. For example, soaps and detergents lower the surface tension of water to a marked degree and thus improve the spreading property of these substances. In order to enable preparations like tooth-pastes, mouth-washes, nasal jellies, toilet creams, and medicinal emulsions to spread evenly synthetic detergents are added to them.

There is a rough parallelism between volatility and surface tension. Volatility measures the relative tendency of molecules to enter the gas phase as opposed to the liquid phase. Surface tension measures the tendency of molecules to enter the surface of the liquid as opposed to the bulk liquid.

We note that the surface tension varies between 10 to 500 erg/cm². What does this mean in terms of energy required to bring a mole of molecules from the interior of a liquid to the surface? Typical surface area of small molecules being in the neighbourhood of 10^{-14} cm², there are about 10^{14} molecules per cm² of surface. For a value of $\gamma = 10$ erg/cm² (a typical value for such molecules) we obtain 10^{-13} erg per molecule or about 1 kcal per mole. Heats of vapourisation (see Table 8.1) are usually a few kilocalories per mole; consequently, the energy necessary to create a new surface averages about 10 to 50 per cent of the energy necessary to free the molecule completely from the condensed phase.

8.5 VISCOSITY

Flow is a characteristic property of a liquid. Some liquids, like castor oil flow slowly, while some others like kerosene flow rapidly. These differences in flow rates result from a property known as viscosity. *Viscosity* is the resistance of a liquid to flow. It is a frictional effect due to passage of one layer of liquid over another and is sometimes referred to as internal friction.

Let us examine the motion of a liquid on a glass plate. The liquid may be considered to be consisting of a number of molecular layers arranged one over another. The layer in contact with the glass plate remains stationary, the second layer moves a little quicker than the first and the third layer moves quicker than the second. There is thus a movement of different layers past one another in the direction of the flow. The displacement of different layers relative to one
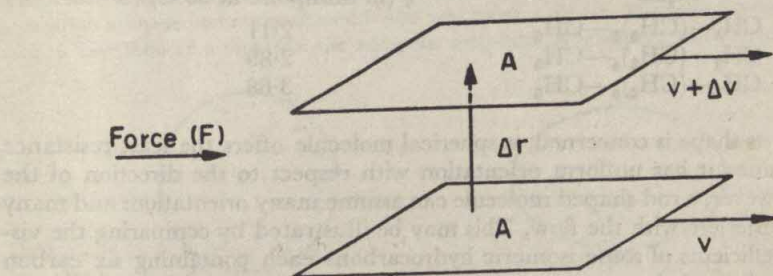
Fig. 8.11 Two parallel liquid layers, each of area A, separated by a distance Δr. F is the tangential force which maintains the velocity difference ΔV between the layers. The coefficient of viscosity (η) is defined by the relation, $\eta = F/(\Delta V/\Delta r)A$.

another is opposed by the internal friction of the liquid. When the flow of the liquid becomes steady, there will be a constant difference in the velocity between two different layers (Fig. 8.11). It has been found that the tangential (or shearing) force per unit area required to maintain this condition is directly proportional to the difference in velocity between two adjacent layers and inversely proportional to the distance between them (Fig. 8.11). We define the *viscosity coefficient*, η, as the force per unit area required to maintain unit difference in velocity between two parallel layers in the liquid one centimetre apart. The coefficient of viscosity is expressed in dynes/cm². Viscosity is expres-

sed in units called poise named after Poiseuille. The reciprocal of the coefficient of viscosity $(1/\eta)$ is called *fluidity*.

Viscosity is markedly dependent on temperature. As the temperature of a liquid increases, its viscosity decreases. The decrease in viscosity is of the order of about 2 per cent per degree centigrade rise in temperature. The viscosity coefficients in centipoises of several liquids at different temperatures are given in Table 8.3.

Table 8.3 Viscosity Coefficients of Some Liquids (centipoise)

Liquid	0°C	20°C	40°C	60°C	80°C
Benzene	0·912	0·652	0·503	0·392	0·329
Carbon tetrachloride	1·329	0·969	0·739	0·585	0·468
Ethyl ether	0·284	0·233	0·197	0·140	0·118
Ethyl alcohol	1·773	1·200	0·834	0·592	—
Water	1·792	1·002	0·656	0·469	0·357

Viscosity of a liquid is also dependent on factors like molecular size and shape. We would expect a larger molecule to offer more resistance to flow than a smaller one. This is supported by the η values of a few liquids as shown below:

Liquid	η (in millipoise at 30°C)
$CH_3-(CH_2)_3-CH_3$	2·11
$CH_3-(CH_2)_4-CH_3$	2·89
$CH_3-(CH_2)_5-CH_3$	3·68

As far as shape is concerned, a spherical molecule offers the least resistance to flow since it has uniform orientation with respect to the direction of the flow. However, a rod-shaped molecule can assume many orientations and many of these interfere with the flow. This may be illustrated by comparing the viscosity coefficients of some isomeric hydrocarbons each containing six carbon atoms as shown below:

Hydrocarbon	η (in millipoise at 25°C)

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ 3·29
    n-hexane

$\quad\quad\quad CH_3$
$\quad\quad\quad |$
$CH_3-CH_2-CH-CH_2-CH_3$ 3·07
  3-methyl pentane

$\quad\quad CH_3$
$\quad\quad |$
$CH_3-CH-CH-CH_3$ 2·95
$\quad\quad\quad |$
$\quad\quad\quad CH_3$
  2, 3-dimethyl butane

8.6 ORIGIN OF INTERMOLECULAR FORCES IN LIQUIDS

We have made frequent references earlier to the fact that attractive forces exist between molecules. These forces are responsible for liquefaction of gases and also for holding the molecules of the liquid in a confined space. We shall now briefly consider various types of interactions between molecules which are responsible for these forces.
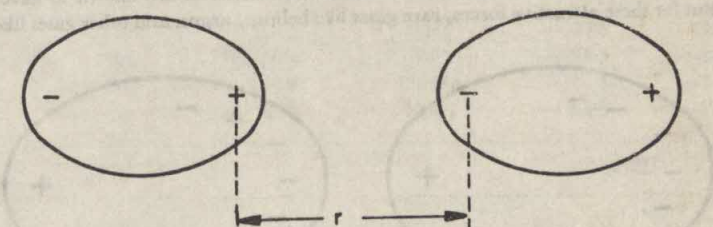
Fig. 8.12 Dipole–dipole interaction

Dipole–dipole interaction: When a liquid contains molecules with permanent dipole moments, the molecules interact with one another. The positive end of one molecule attracts the negative end of another molecule or vice versa. The force of attraction is electrostatic in nature. The orientation of molecular dipoles is such that the ends of similar charges are as far apart as possible (Fig. 8.12).

Dipole-induced dipole attraction: When a molecule with permanent dipole approaches a non-polar molecule, the dipole of the first molecule interacts with the electron cloud of the non polar molecule or atom causing a distortion. The ease with which the distortion can be brought is expressed as *polarisability* usually denoted by *a*. As a result of this distortion there will be charge separation in the second molecule and it also behaves as a dipole. The polar molecule is then said to have induced a dipole in the non-polar molecule. A schematic representation of this

non-polar molecule   Polar molecule
(symmetrical charge distribution)   (unsymmetrical distribution of charge)
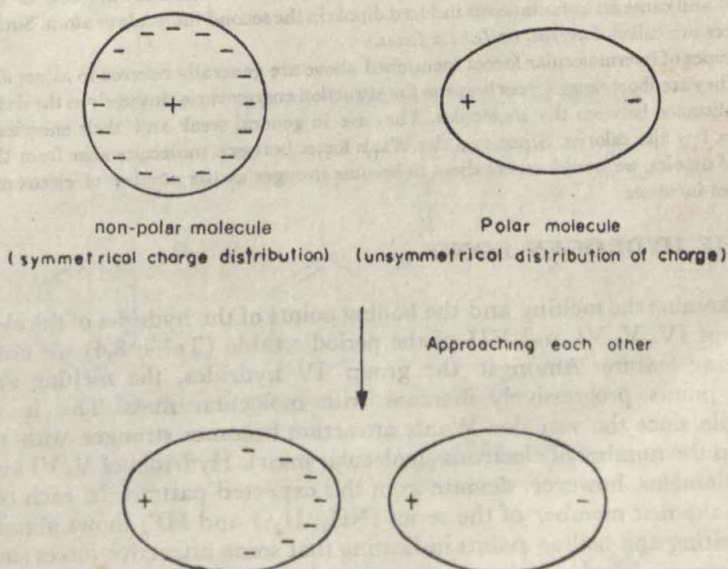
Fig. 8.13 Dipole–induced dipole interaction

interaction is shown in Fig. 8.13. This is analogous to the attraction of a soft iron piece by a magnet. The north pole of the magnet induces a south pole in the soft iron piece. There will then be attraction between the opposite poles.

Induced dipole–induced dipole attraction: In permanent dipoles, it is easy to see how the positive end of one molecule attracts the negative end of another molecule. Even neutral molecules and atoms where the charge distributions are symmetrical are known to have attractive forces. But for these attractive forces, rare gases like helium, argon and other gases like hydrogen

Induced charge   Instantaneous preponderance
Separation   of negative charge
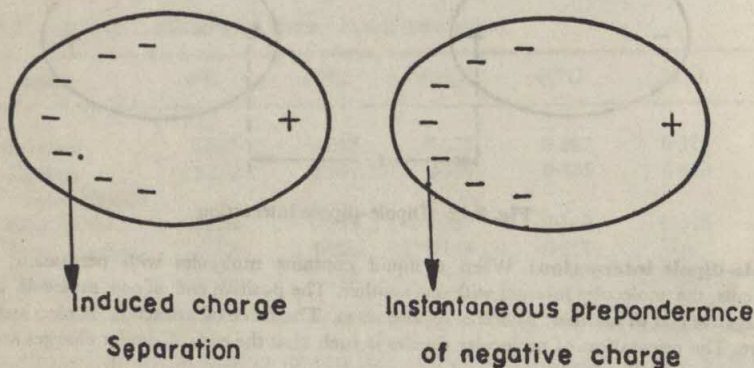
Fig. 8.14 Induced dipole–induced dipole interaction

and nitrogen could not have been liquefied. Molecules and atoms are neutral in the sense that the electrons are uniformly distributed around the nuclei. That is, the centre of negative charges coincides with the centre of positive charges. If, however, the electron cloud at any instance is even slightly displaced relative to the positive centre, a small instantaneous dipole is developed. This instantaneous dipole can interact with a nearby neutral atom or molecule as shown in Fig. 8.14 and cause an instantaneous induced dipole in the second molecule or atom. Such attractive forces are called *dispersion* or *London forces*.

The types of intermolecular forces mentioned above are generally referred to as *van der Waals forces*. They are short range forces because the attraction energy varies inversely as the sixth power of the distance between the molecules. They are in general weak and their energies seldom exceed a few kilo calories. Since van der Waals forces between molecules arise from the inter-action of dipoles, we would expect them to become stronger as the number of electrons in the molecules increases.

8.7 THE HYDROGEN BOND

If we examine the melting and the boiling points of the hydrides of the elements of groups IV, V, VI and VII of the periodic table (Table 8.4) we notice an interesting feature. Amongst the group IV hydrides, the melting and the boiling points progressively increase with molecular mass. This is under-standable since the van der Waals attraction becomes stronger with the in-crease in the number of electrons (molecular mass). Hydrides of V, VI and VII group elements, however, deviate from this expected pattern. In each of these groups, the first member of the series (NH_3, H_2O and HF) shows abnormally high melting and boiling points indicating that some attractive forces (in addi-tion to van der Waals type) must be present in these hydrides. This interaction has been traced to the special ability of the hydrogen atom in such molecules

Table 8.4 Melting and Boiling Points of Hydrides of Groups IV to VII Elements of the Periodic Table

Group IV			Group V		
	MP (°C)	BP (°C)		MP (°C)	BP(°C)
CH_4	−184	−161·5	NH_3	− 77·3	−33·4
SiH_4	−185	−111·8	PH_3	−135·0	−88·0
GeH_4	−165	− 90·0	AsH_3	−113·5	−55·0
SnH_4	−150	− 52·0	SbH_3	− 88·0	−17·0

Group VI			Group VII		
	MP (°C)	BP (°C)		MP (°C)	BP (°C)
H_2O	− 0·0	100·0	HF	− 92·3	19·4
H_2S	− 82·9	− 61·8	HCl	−112·0	−83·7
H_2Se	− 64·0	− 42·0	HBr	− 88·5	−67·0
H_2Te	− 51·0	− 2·0	HI	− 50·8	−36·0

to form a bridge between two highly electronegative atoms. This type of bond is called the *hydrogen bond* and it is represented as in Fig. 8.15.
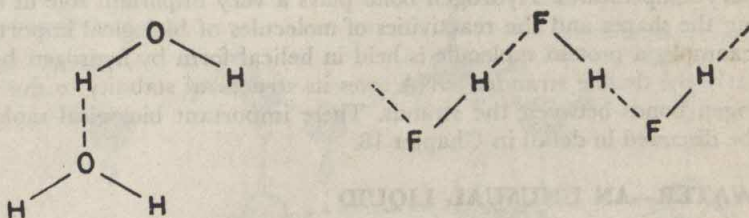
Fig. 8.15 Hydrogen bonded structures of H_2O and HF
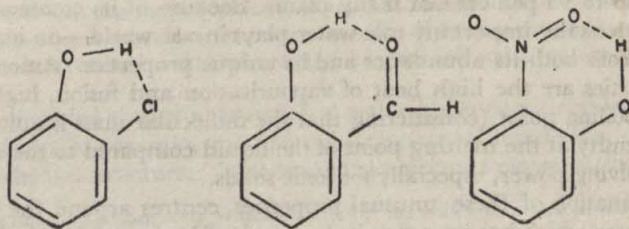
Fig. 8.16 Intramolecular hydrogen bonds
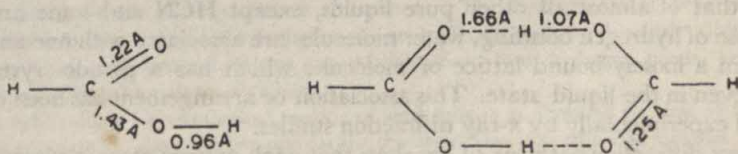
Fig. 8.17 Hydrogen bonding in formic acid

Since the hydrogen atom (with only a single $1s$ orbital available) cannot form more than one covalent bond, the simplest explanation of the hydrogen bond would be in terms of the electrostatic effect. When a hydrogen atom is attached to a highly electronegative atom, the electron pair is unevenly shared and this creates a positive charge on the hydrogen atom and this in turn attracts the negative end of other molecules. In many cases, the unshared electron pair of the attracted atom approaches the hydrogen atom (which has a formal positive charge) to form the hydrogen bond.

The examples of water and hydrofluoric acid given earlier show *intermolecular bridges. Intramolecular hydrogen bonding* is also a common phenomenon, and some examples are given in Fig. 8.16. Intramolecular hydrogen bonding has little effect on the melting and the boiling points of a substance, but appreciably affects its reactivity.

In intramolecular as well as intermolecular hydrogen bonds, some distortion of the molecule is inevitable. Thus, the bond lengths of an isolated molecule of formic acid are different from those in the hydrogen bonded dimer (Fig. 8.17). We see that the O—H bond gets stretched by about 10 per cent due to hydrogen bond formation.

Compared to the ordinary covalent and ionic bonds, hydrogen bonds are weak bonds with typical values of energies in the range of 3–10 kcal/mol. Nevertheless, since this value is 10–15 times the thermal energy at room temperature, hydrogen bonded structures are quite stable against dissociation at ordinary temperatures. Hydrogen bond plays a very important role in determining the shapes and the reactivities of molecules of biological importance. For example, a protein molecule is held in helical form by hydrogen bonds; similarly the double stranded DNA owes its structural stability to the strong hydrogen bonds between the strands. These important biological molecules will be discussed in detail in Chapter 18.

8.8 WATER—AN UNUSUAL LIQUID

Perhaps no chemical substance is so well-known to us as water. It is a major component in all living organisms, constituting about 65 per cent of the human body and up to 95 per cent of many plants. Because of its commonness, we tend to overlook the important role water plays in our world —an importance that stems from both its abundance and its unique properties. Among its unusual properties are the high heat of vapourisation and fusion, high specific heat, high boiling point (considering that the molecular mass is quite small), the great density at the melting point of the liquid compared to the solid and higher dissolving power, especially for ionic solids.

The explanation of these unusual properties centres around the structure of liquid water which has an extensive network of hydrogen bonds. We know that water is a polar molecule; in fact, the dielectric constant of water is higher than that of almost all other pure liquids, except HCN and some amides. Because of hydrogen bonding, water molecules are associated with one another to form a loosely bound lattice of molecules which has a pseudo-crystalline form even in the liquid state. This association or arrangement has been determined experimentally by x-ray diffraction studies.

X-ray diffraction patterns of ice show that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 2·76 A (Fig. 8.18).

Hydrogen bonds hold the oxygen atoms together leading to a very open structure.* Similar studies of liquid water near its melting point reveal that the number of nearest neighbours is between four and five. From this information it
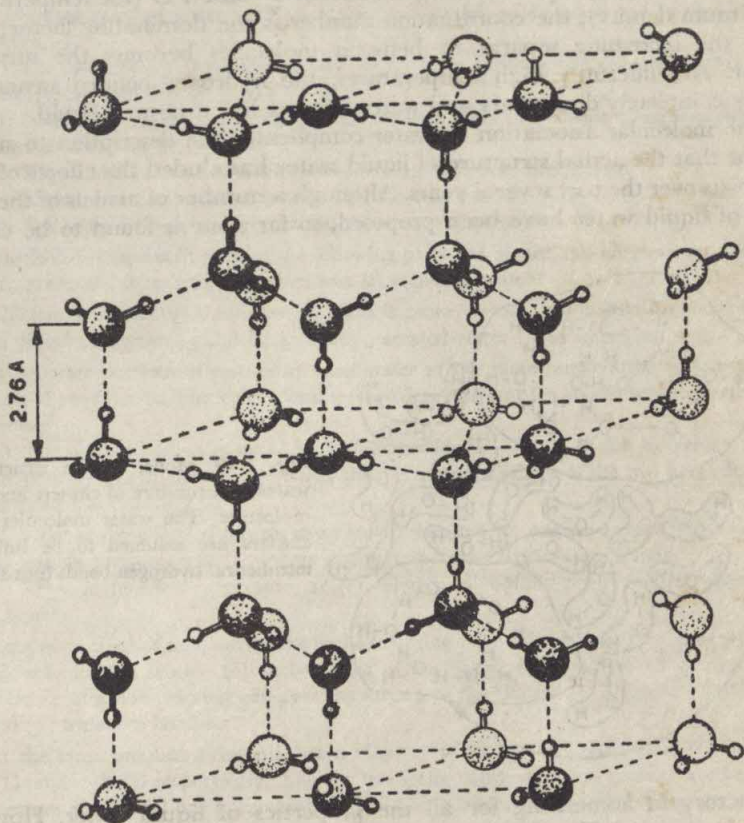
Fig. 8.18 The structure of ordinary ice crystals. There is one proton along each oxygen–oxygen axis closer to one or the other of the two oxygen atoms. The locations of hydrogen atoms are not given by x-ray diffraction but are assumed.

may be concluded that the structure of water bears considerable resemblance to that of ice. Apparently, melting results in partial breakdown of the rather open tetrahedral structure. This breakdown permits closer packing, although

* Such a structure is consistent with the model of the water molecule in which the oxygen atom is assumed to have four sp^3 hybrid orbitals. Two of these hybrid orbitals contain lone-pair electron while the other two, each containing a single electron, are utilised to overlap with the $1s$ orbitals of two hydrogen atoms (Chapter 4). The hydrogen bond between water molecules is formed between the hydrogen of one molecule and the lone-pair electrons of another. Thus, each water molecule can participate in four hydrogen bonds, two as a hydrogen donor and two as an acceptor.

The void volume for tetrahedral packing of hard spheres is about 66 per cent of the total volume compared to about 26 per cent for the closest-packing (coordination number 6). H_2S crystallises in a closed-packed arrangement. The density of water would be about two if it had a closed-packed structure of spherical molecules of diameter 2·76 A.

water is, of course, far from being a closed-packed structure. As the temperature is raised the number of near neighbours increases, but at the same time the distance between adjacent molecules increases. The net result is the well-known increase in density upon melting. Between 0° and 4°C (the temperature of maximum density), the coordination number is the dominating factor; above 4°C, the increasing separation between molecules becomes the important factor. At sufficiently high temperatures, the hydrogen-bonded structure of water completely disappears and water behaves like a normal liquid.

The molecular association in water complicates the description to such an extent that the actual structure of liquid water has eluded the efforts of many chemists over the past several years. Although a number of models of the structure of liquid water have been proposed, so far none is found to be entirely
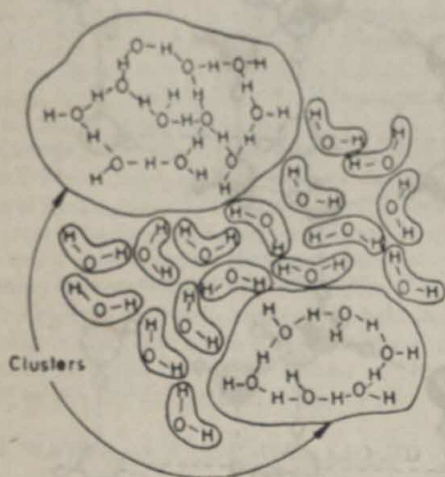
Fig. 8.19 Model of the structure of water as a mixture of clusters and single molecules. The water molecules in the clusters are assumed to be linked by tetrahedral hydrogen bonds (not shown).

satisfactory in accounting for all the properties of liquid water. However, the cluster-model (Fig. 8.19) merits mention because of its simplicity. In this model, the liquid is regarded as a mixture of ' clusters ' of water molecules (where each molecule is linked to four others) and single water molecules (which occupy the spaces between the clusters). The clusters are continuously built up and broken down and single molecules are, therefore, added on or split off in this rapid exchange process. Water molecules with one, two or three hydrogen bonds are also present at the surface of the clusters, although only as short-lived intermediates states. Calculations show that the proportion of hydrogen bonds broken during melting of ice is about 50 per cent.

SUGGESTED READING

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PROBLEMS

8.1 Explain the following:

(a) The boiling point of a liquid rises on increasing pressure.

(b) Drops of liquid assume spherical shape.

(c) boiling point of water (100°C) is abnormally high when compared to that of H_2S (−61·8°C).

(d) The temperature of the liquid does not rise at its boiling point although heat is being continuously supplied.

(e) Level of mercury in a capillary tube is lower than the outside when a capillary is inserted in mercury.

(f) Liquid helium has a smaller surface tension than does liquid neon.

(g) Liquids like ether and acetone are kept in cool places.

(h) Tea or coffee is sipped from a saucer when it is quite hot.

8.2 Which of the liquids in each of the following pairs has higher vapour pressure: (a) alcohol, glycerine; (b) petrol, kerosene; and (c) mercury, water?

8.3 Which one in each of the following pairs is more viscous: (a) coconut oil, castor oil; (b) glycerine, kerosene; and (c) soft drink, aerated water (soda water)?

8.4 (i) Separate portions of chloroform and water at the same temperature are poured on each of your hands. The chloroform feels colder. Account for this in terms of attractive forces.

(ii) The normal boiling point of hydrogen chloride is −84°C. At this temperature vapour pressure of sulphur dioxide is less than 10 mm. In which of the two intermolecular attractions are stronger?

8.5 (i) What is the effect of temperature on (a) density; (b) surface tension; (c) viscosity; (d) vapour pressure; and (e) energy distribution in the molecules of a liquid?

(ii) What is the effect of pressure on (a) volume; (b) boiling point; and (c) viscosity of a liquid?

8.6 State what effect, if any, variations in the following have on the boiling point of a liquid: (a) volume of a liquid; (b) surface area of the liquid; (c) atmospheric pressure; (d) presence of a non-reacting gas over the surface of the liquid; (e) intermolecular forces; and (f) hydrogen bonding.

8.7 At the same pressure ammonia has a viscosity of $91·8 \times 10^{-8}$ and $31·7 \times 10^{-4}$ poise at 0°C and −50°C respectively. Explain this large difference. Since water at the same pressure and at 0°C has a viscosity of $179·3 \times 10^{-4}$ poise, explain why water has a much higher viscosity than ammonia.

8.8 Given below are vapour pressure values for a liquid X at several temperatures.

Temp °C	38	70	90	100	150	180	187	191	195
Vapour pressure mm	1	11	27	43	285	582	700	760	850

(a) What is the normal boiling point of water?

(b) Is the normal boiling point of X higher or lower than that of water?

(c) What will be its boiling point at a hill station where the pressure is 700 mm?

(d) Are the intermolecular forces in X stronger or weaker than in water?

8.9 At what temperature will water boil when the elevation is such that the barometric pressure is 500 mm?

(HINT: The variation of vapour pressure (P) of a liquid with temperature is given by the equation

$$\log P = \frac{-A}{T} + B = \frac{-\Delta H}{2 \cdot 303 RT} + B$$

where ΔH is the molar heat of vapourisation of the liquid and R the gas constant. Therefore,

$$\log \frac{P_2}{P_1} = \frac{\Delta H}{2 \cdot 303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

where P_2 and P_1 are the vapour pressures at temperatures T_2 and T_1.

8.10 In a 1 litre flask 100 ml of carbon tetrachloride are placed at a temperature of 35°C. If vapour pressure of carbon tetrachloride be 176 mm at this temperature, what weight of carbon tetrachloride vapour is present in the flask?

8.11 A drop of water (0·050 cc) is injected into a 1 litre box that is completely evacuated. If the temperature of the system is kept at 27°C how much liquid water will be lost when equilibrium is established? The density of liquid water at 27°C is 0·9965 g/cc. The equilibrium vapour pressure of liquid water at 27°C is 26 mm. Assume ideal behaviour of the gas.

8.12 At 25°C, 10 litres of dry air is bubbled slowly through 115·2 g of a pure liquid whose molecular mass is 120 g/mol. The remaining liquid weighed 113·1 g. Assuming the vapour to behave ideally and the volume to be approximately equal to that of the dry air calculate the vapour pressure of the liquid.

8.13 Benzene has a density of 0·879 g/ml and has a surface tension of 28·88 dyne/cm at 20°C. What will be the difference of its heights in two capillaries of radii 0·1 mm and 0·15 mm? ($g=981$ cm/s^2).

(HINT: The equilibriun condition in the capillary rise method is given by the equation $\gamma = \frac{1}{2} r h \rho g$, where γ is the surface tension of the liquid, r the radius of the capillary, h the height to which the liquid of density ρ rises, and g the acceleration due to grainty.)

8.14 A U-tube containing water at 20°C has capillary arms of different radii, one equal to 2 mm and the other equal to 5 mm. Calculate the difference in the levels of the two arms. Water has a density of 0·998 g/cc and surface tension 72·75 dyne/cm at 20°C. Calculate the difference in levels if the U-tube contains acetone at 20°C. Acetone has a density of 0·792 g/cc and a surface tension of 23·7 dyne/cm at 20°C.

8.15 How high will sap rise in a plant if the capillaries are 0·01 mm diameter, the density of the fluid is 1·3 g/cc and its surface tension 65 dynes/cm?

8.16 In a measurement of viscosity by Ostwald viscometer at 20·2°C water takes 30 s to flow between the upper and lower marks while the flow of another liquid of density 1·50 g/cc takes 35 s. Taking density of water at 20·2°C to be 0·9982 g/cc and its viscosity 1·001 centipoise, calculate the viscosity of the other liquid.

(HINT: If t_1 and t_2 are the times taken by identical amounts of two liquids (densities ρ_1 and ρ_2) to flow between two fixed marks of a viscometer, then their viscosities η_1 and η_2 are related by the expression $\eta_1/\eta_2 = t_1 \rho_1 / t_2 \rho_2$.)

8.17 Equal volumes of water and isopropyl alcohol were found to weigh 9·982 and 7·887 g respectively at 20°C. At the same temperature isopropyl alcohol flows through a viscometer in 624 s and an equal volume of water flowed through the same viscometer in 200 s. If the viscosity of water at 20°C is 10·087 millipoise calculate the viscosity of isopropyl alcohol at the same temperature.

9

Chemical Thermodynamics

> ...the deep impression which...thermodynamics made upon me....It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown....
>
> ALBERT EINSTEIN

> ...thermodynamics is an instrument of great power and universality. It shows the engineer the maximum amount of work which a given quantity of fuel can produce in a given type of steam engine....
>
> To the manufacturing chemist thermodynamics gives information concerning the stability of his substances, the yields which he may hope to attain, the methods of avoiding undesirable substances, the optimum range of temperature and pressure, the proper choice of solvent, the limitations of methods of fractional distillation and crystallisation.
>
> To the analytical chemist it offers the means of predicting the limits of possible error, of avoiding side-reactions, of choosing the concentrations best suited to his work....
>
> G. N. LEWIS AND M. RANDALL

The subject of thermodynamics deals with the laws governing the energy interchanges in macroscopic phenomena. Its three central principles, commonly known as the three laws of thermodynamics, find numerous applications in inorganic, organic, analytical and biochemistry and constitute one of the most important links between the different branches of chemistry. Indeed, the usefulness of thermodynamics ranges beyond chemistry and the subject is equally important to a physicist, a biologist or an engineer. It may be justifiably said that thermodynamics provides one of the great unifying themes for all natural sciences.

The restriction of thermodynamics to macroscopic phenomena arises because all the concepts that enter in this theory are directly related to the observable features of matter in bulk. This restriction is both the strength and the weakness of the subject. On the one hand, by limiting itself to finding relations between only measurable quantities, thermodynamic principles enjoy a permanence seldom shared by other scientific theories. On the other hand, by avoiding the

use of microscopic concepts, the laws of thermodynamics fail to provide as deep an insight as the atomic-molecular approach. Although thermodynamics has developed essentially as a phenomenological theory, the modern practice is to occasionally combine its macroscopic arguments with microscopic interpretation. We shall also follow this mixed approach wherever it simplifies the understanding of a particular phenomenon or a particular concept.

9.1 BASIC DEFINITIONS AND CONCEPTS

In this section, we shall define and explain some of the basic concepts which are needed to formulate and apply the laws of thermodynamics.

9.1.1 System and Surroundings

The part of the physical universe which is under study is referred to as *system* while the rest of the universe is called the *surroundings*. Such distinction is implicit in all scientific analysis but it assumes great significance in thermodynamics as we shall find in the following sections. A thermodynamic system must necessarily be macroscopic, i.e. from a microscopic view point the system must contain a large number of particles.* A system is separated from the surroundings by *boundaries* which may be real (fixed or movable) or which may be imaginary. Further boundaries may be considered part of either the system or the surroundings, depending upon convenience.

For example, we can study the behaviour of a certain amount of gas by enclosing it in a container, say a cylinder. The walls of the cylinder are then the boundaries which separate the system (i.e. the gas) from the surroundings. If the walls are rigid, then the cylinder does not influence the behaviour of the gas and it is convenient to consider the boundaries as part of the surroundings. If the cylinder is equipped with a piston, then the system has obviously movable boundaries. Instead of rigid walls, if the container has elastic walls ˙(e.g. a balloon or a rubber vessel) then some aspects of gas behaviour, like change in volume on application of pressure, would also be dependent on the elastic properties of the wall material. In such a case, it is more convenient to regard the gas and the container as the system.

A system is said to be *isolated* if it can neither exchange matter nor energy with the surroundings. It follows that surroundings do not influence the behaviour of an isolated system. A system is *closed* if it can exchange energy with the surroundings but not matter whereas an *open* system exchanges both matter and energy with the surroundings.

A sample in a sealed thermos flask made of perfect insulating material is a simple example of an isolated system. To the extent that the universe has no surroundings (by definition), the universe is also an isolated system. A sealed tube is an example of a closed system while samples in open vessels represent open systems. All organisms (plant, animal, man) are open systems from the thermodynamic viewpoint since they exchange matter (food, waste products) and energy with the surroundings.

*It turns out that thermodynamic quantities represent averages over atomic-molecular quantities. For example, temperature is a measure of average kinetic energy of atoms and molecules. Obviously, there should be a sufficiently large number of particles in a system to make averages meaningful. A more precise statement is that the fluctuation from the average value should be negligible compared to the average value. Systems containing particles of the order of 10^{23} easily satisfy this requirement.

9.1.2 Thermodynamic State

The state of a thermodynamic system is defined by specifying the values of various (macroscopic) properties. The latter are usually called *state variables* or *state functions*. It is a matter of experience that all state variables are not independent because algebraic relationships—known as *equations of state*—exist between the different state variables. Consequently the state of a system is uniquely specified by giving the values of a few variables only. In other words, once the values of the independent state functions of a system are fixed, the state of the system is fixed and all the other (dependent) state variables assume definite values.

For an ideal gas, the equation of state is $PV=nRT$ (Chapter 6). Thus, out of the four variables P, V, n and T only three can be independently varied. In addition to these, we shall come across several more variables which also depend only upon the state of the system. It can be shown that when any three state variables of an ideal gas are specified, all other state variables of the system get simultaneously fixed.

9.1.3 Equilibrium and Non-equilibrium Phenomena

There are situations where a system may not have a definite state. It follows that in these situations state variables cannot have definite values. Whenever this happens, we say that the system is not in equilibrium. A system in *equilibrium* is characterised by state variables which do not change in time and space. An important restriction of thermodynamics is that it deals only with equilibrium states.*

To illustrate non-equilibrium phenomena, consider the following example. Take a sample of gas in a cylinder fitted with a piston and attach a barometer and a thermometer to the system—we find that the gas has a definite pressure and temperature. However, if the piston is moved suddenly, then the equilibrium state is disturbed and for a while the barometer and the thermometer will not register any definite reading. Once the system settles down to a new equilibrium state, the gas will again acquire a definite pressure and temperature which will not change unless the gas is disturbed anew.

9.1.4 Thermodynamic Potentials

Just as gravitational and electrostatic potentials control equilibrium in gravitational and electrostatic fields, thermodynamic potentials govern equilibrium in thermodynamic systems. For instance, if the pressure within a system is not uniform, movement of matter will take place from regions of higher pressure to those of lower pressure and hence the system will not be in equilibrium. Similarly, non-uniformity of temperature will cause heat to flow from one part of the system to another and once again there will be a non-equilibrium situation. Pressure and temperature are thus examples of thermodynamic potentials which decide the existence or otherwise of mechanical and thermal equilibrium.

A very important potential for the chemist is the chemical potential which controls the chemical equilibrium between different species. If the chemical potential of every species in a system is not uniform, reactions occur and they proceed until the chemical potential becomes

*The fact that time is never a variable in its equations means that there is no ' dynamics ' in thermodynamics. In the opinion of many, the subject should be more appropriately called as *thermostatics* but this suggestion has never been popular. The current name has originated because of the intimate connection of this subject with steam engines during the early years of its development.

21

uniform. The student will encounter and appreciate the full power and elegance of the chemical potential approach to chemistry in the study of advanced chemical thermodynamics.

9.1.5 The Nature and Types of Processes

We have so far been considering equilibrium within a system. We next consider equilibrium between a system and its surroundings. If a particular potential does not have equal value inside and outside a system, there takes place a transport of matter and/or energy across the boundaries. The direction of transport, of course, depends upon the relative values of the inside and outside potentials. When interaction with the surroundings ceases, the system attains a new equilibrium state specified by new values of state variables. Thus the surroundings by interacting with a system enable the latter to transform its state. The transition from one equilibrium state (initial state) to another (final state) is called a *process*. It is important to realise that thermodynamics provides no information about rate and mechanics of transition, but it gives precise information about the relationship between the state variables of the initial and final states. It can also forecast whether a given transition is possible or not though it cannot tell whether an allowed transition would be slow or fast. The ability to rationalise and predict the direction of physico-chemical transformations and the ability to relate the state functions of the initial and final states, are the two most important features of thermodynamics useful to chemists.

A system can usually change from one equilibrium state to another through a variety of routes. In other words, there can be a number of processes connecting an initial state to a final state. If temperature remains constant throughout the transformation, it is said to be an *isothermal* process. In *isobaric* and *isochoric* processes, pressure and volume respectively are maintained constant, while in *adiabatic* processes, no heat is exchanged between the system and the surroundings. The process which brings back a system to its original state after a series of changes, is called a *cyclic process*.

A special type of process which is crucial for the understanding of many thermodynamic arguments is the so-called *reversible* process. In a reversible process the initial and the final states are connected through a succession of equilibrium states, i.e. at every state along a reversible path, there exists an equilibrium between the system and the surroundings. Reversible processes are also called quasi-static processes. It should be noted that reversibility is only an idealisation, albeit an useful one; actual processes in nature are invariably irreversible, in the sense that equilibrium is not maintained during the transformation process. (Even for irreversible processes, the initial and final states must, of course, be equilibrium states.) Since a clear appreciation of the subtle concept of reversibility holds the key to the successful application of thermodynamic reasoning to many problems—especially those involving the second law of thermodynamics—we shall return to this topic in greater detail later in this chapter.

9.1.6 State Functions

Inasmuch as state functions depend only on the state of a system, it should be obvious that the change in any state function should be uniquely determined by the initial and the final state. For instance, if the pressure and temperature in the initial state are P_1 and T_1 and that in the final state are P_2 and T_2,

then the difference ΔP $(=P_2 - P_1)$ or ΔT $(=T_2 - T_1)$ is independent of the path followed (Fig. 9.1). The importance and the usefulness of state functions arise primarily because the details of the transformation process are irrelevant to calculate changes in state functions as long as the initial and the final states are known.

Fig. 9.1 There are infinite number of paths which connect a given initial state to a given final state. This figure shows three paths connecting state 1 to state 2. The differences $P_2 - P_1$ and $T_2 - T_1$ are independent of this path since pressure and temperature are state functions.
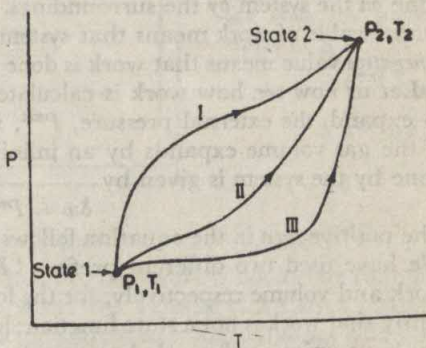
Let us consider a simple analogy to bring out the meaning of state function. Suppose the roof of a building is 150 ft above the ground floor. A person can go from the ground floor to the roof by several alternate routes. He can use a rope to climb the wall or use a staircase or a lift and so on. He may even use a helicopter to go above the top and then jump down. But no matter how he reaches the roof the change in elevation will remain 150 ft. Elevation is thus a state function. The magnitude of effort (or exhaustion) will, however, depend upon the path; the extent of exhaustion, therefore, is not a state function.

9.1.7 Extensive and Intensive Quantities

All quantities, irrespective of whether they are state variables are not, can be classified as either *extensive* or *intensive*. Extensive quantities are additive while intensive quantities are not. For example, if two systems are joined together, their volumes will add but their temperatures will not. In particular, if the temperature of the two systems is the same, the temperature of the joint system will also be the same. But if the volumes are equal, the joint system will have double the volume. Temperature is thus an intensive and volume an extensive quantity.

9.2 THE NATURE OF WORK AND HEAT

In order to formulate the first law of thermodynamics it is necessary to first examine the nature of work and heat.

9.2.1 Work

Work is one of the modes by which a system can exchange energy with the surroundings. Consider a certain amount of gas enclosed in a cylinder fitted with a movable, frictionless* piston. If the internal (gas) pressure on the piston is greater than the external (surroundings) pressure, the piston will move out,

*If the piston is not frictionless, part of the energy exchange will be in the form of heat. Since we wish to consider here energy transfer only in the form of work, we ' invent ' a ' frictionless ' piston. This is another of the thermodynamic idealisations which does not exist in nature but is very useful for theoretical arguments.

pushing back the surroundings. In the process, the system loses energy to the surroundings. The loss in energy by the system is equal to the work done *by* the system *on* the surroundings. If the external pressure is greater than the internal pressure, the piston will move down and the surroundings will lose energy to the system. This gain in energy by the system is equal to the work done *on* the system *by* the surroundings. We shall follow the convention that a *positive* value of work means that system does work (i.e. it loses energy) while a *negative* value means that work is done on the system (i.e. it gains energy).*

Let us now see how work is calculated for an expansion process. For a gas to expand, the external pressure, P^{ext}, must be less than the gas pressure, P. If the gas volume expands by an infinitesimal amount dV, then the work δw done by the system is given by

$$\delta w = P^{ext} \, dV$$

The positive sign in the equation follows from the convention we have adopted. We have used two different prefixes ' δ ' and d to indicate small changes in work and volume respectively, for the following reason. It will be shown presently that work is not a state function; hence, amount of work, in general, does not have unique value. (It has unique value only when the path is specified.) On the other hand, volume being a state function, change in it, including infinitesimal changes, has unique value irrespective of the path. We shall use in this book the prefix ' d ' to indicate infinitesimal change and Δ to indicate finite change in a state function while δ will be used to indicate small (arbitrary) change in other variables. No prefix will be used to indicate finite changes in quantities which are not state functions. It is important to note that work done depends on the pressure exerted on the system by the surroundings and not on the pressure in the system. Only in an equilibrium situation are the two pressures equal. During expansion and compression, these two pressures have to be necessarily unequal; under these conditions we use the surrounding pressure to calculate work.

It is easy to understand the form of the above equation. We know from mechanics that when a body is displaced by an infinitesimal distance dx, by an impressed force F^{ext}, then the work (δw) involved is

$$\delta w = F^{ext} \, dx$$

The same equation is valid for the movement of the piston under the impressed force of the surroundings. However, since pressure is defined as force per unit area (see Chapter 6), the force due to the surroundings on the piston is equal to the surroundings pressure (P^{ext}) multiplied by A, the surface area of the piston (Fig. 9.2), i.e.

$$F^{ext} = P^{ext} A$$

From the above two equations, it follows that

$$\delta w = F^{ext} \, dx = P^{ext} A dx = P^{ext} (A dx) = P^{ext} \, dV$$

where dV is the change in volume when a piston with surface area A is displaced by a distance dx.

For finite changes, the equation for work (w) is written as

$$w = \int \delta w = \int_{1}^{2} P^{ext} \, dV$$

where 1 and 2 represent the initial and final states of the expansion process and the integral sign represents the sum over the infinitesimal steps. (State

*Some books use the opposite choice for the sign of work. However, final results do not depend upon the choice as long as it is used consistently throughout.
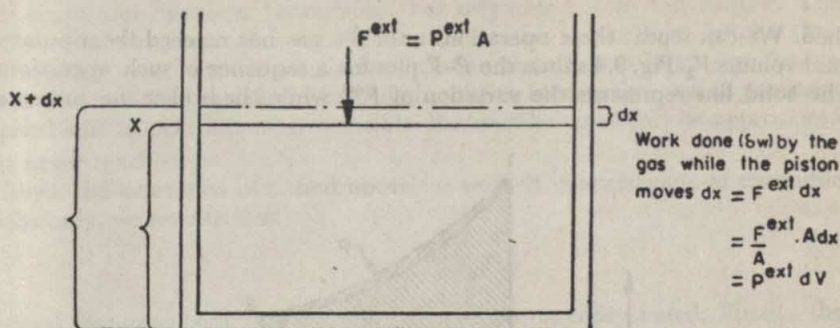
Fig. 9.2 The work done by a gas due to an infinitesimal movement of the piston

symbols over the work integral are omitted because work is not a state function as discussed below.) Consider the case where the volume of a system changes from V_1 to V_2 during expansion with the pressure due to surroundings changing from P_1^{ext} to P_2^{ext}. Consistent with these initial and final states, P^{ext} can be varied in different ways leading to different $P^{ext}-V$ curves and hence different areas. This is illustrated in Fig. 9.3 where the work w (i.e. the area under the $P^{ext}-V$ curve) is shown for two different paths. We see that work depends on how the process is carried out and it is therefore, not a state function.
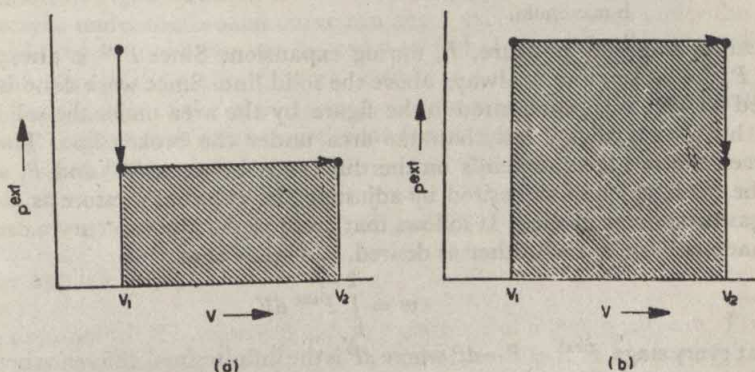
Fig. 9.3 For the same initial and final values of P^{ext} and of volume V, the process can be carried out in two different ways shown above. The work done in each case (given by the shaded area) is different thus showing that work is not a state function.

Reversible expansion: A particular process of interest in thermodynamics is the so-called reversible expansion. The nature of this process is easily understood through an example. Consider again the expansion from V_1 to V_2 of a certain amount of gas enclosed in a cylinder fitted with a piston. If P^{ext} is adjusted to be equal to the gas pressure, P, it is obvious that the piston will neither move up nor down. In other words, the system will remain in equilibrium; the gas neither expanding nor contracting. Let us now decrease P^{ext} very slightly. The gas will now expand until its falling pressure equals the (decreased) external pressure. Expansion will then cease and the gas will reach equilibrium. Again decrease the external pressure by a small amount. The gas will again expand until a new equlibrium state is rea-

ched. We can repeat these operations until the gas has reached the stipulated final volume V_2. Fig. 9.4 shows the $P-V$ plot for a sequence of such operations. The solid line represents the variation of P^{ext} while the broken line indicates
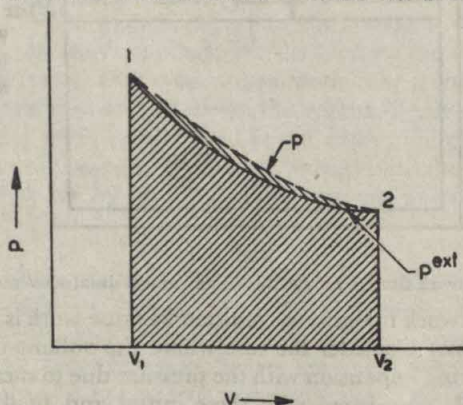
Fig. 9.4 The broken line shows pressure variation for a reversible process while the solid line shows pressure variation for an irreversible process. The area under the solid line is always less than the area under the broken line because work done in a reversible process is maximum.

the variation of gas pressure, P, during expansion. Since P^{ext} is always less than P, the broken line is always above the solid line. Since work done is controlled by P^{ext}, it is represented in the figure by the area under the solid line and this area is always less than the area under the broken line. The gap between the two lines depends on the difference between P^{ext} and P, and it can be made as small as desired by adjusting the external pressure as close to the gas pressure as needed. It follows that areas under the two curves can also be made as close to each other as desired. We know that

$$w = \int_1^2 P^{ext}\, dV$$

But at every stage, $P^{ext} = P - dP$ where dP is the infinitesimal difference between the two pressures. Therefore,

$$w = \int_1^2 (P - dP)dV = \int_1^2 PdV - \int_1^2 dPdV$$

The second integral containing the product of two infinitesimal quantities can be made small enough to be negligible. In the limit therefore,

$$w = \int_1^2 PdV$$

The process we have just described is known as a *reversible process* and the expression derived above gives the work done in a reversible expansion. The definition given earlier namely, that a reversible process consists of a succession of equilibrium states should now be clear. In the limiting case, each infinitesimal step will be an equilibrium state. Further, at each stage the system can be made to expand or contract by infinitesimal adjustment of external pressure. In other words, only infinitesimal change in P^{ext} can reverse the process at

any stage and the term 'reversible' has originated from this feature. The designation quasi-static is sometimes used because it will take infinite time to complete a process in which each (infinitesimal) step is an equilibrium state. As mentioned earlier reversibility is only an idealisation and all processes carried out in practice are irreversible. Reversibility can only be approached but never reached.

Since the expression obtained above for work is characteristic of reversible paths only, we rewrite it as

$$w_{rev} = \int_1^2 P dV$$

Several features about this equation should be carefully noted. Firstly, the pressure in the integral refers to the system pressure. Secondly, the replacement of the surroundings pressure by the system pressure has been possible only because at each stage of this process there is only an infinitesimal difference between the two pressures. Whenever a particular system variable is different from the surroundings variable, a suitable reversible process can be devised which permits the interchange of the variables. Thirdly, even though reversibility restricts the paths, it may still be possible to have several reversible paths connecting the initial and the final states. As such w_{rev} is also not a state function. Finally, a very important result is that w_{rev} gives the maximum work done by a given system for a given expansion. This result follows from inspection of Fig. 9.4. Since for an expansion process, P^{ext} must be less than P, the area under the broken curve can never exceed the area under the solid curve. At the most, the two can be equal (strictly infinitesimally different) and this, therefore, is the mximum work possible.

The application of the above treatment to a compression process should be obvious. We leave this as an exercise for the reader.

Let us now consider some special situations where the two equations

$$w = \int_1^2 P^{ext} dv \quad \text{and} \quad w_{rev} = \int_1^2 P dV$$

can be applied.

Free expansion: This corresponds to expansion of a gas in vacuum. For this obviously irreversible process, $P^{ext}=0$. Hence, $w=0$; that is no work is done in expansion.

Expansion against constant external pressure: This can be done in an irreversible or a reversible manner depending on the circumstances. If a gas whose pressure is different from atmospheric pressure is expanded against the atmosphere this constitutes an irreversible expansion at constant pressure since the atmospheric pressure does not change during the process. The evaluation of the work integral is very simple for this case.

$$w = \int_1^2 P^{ext} dV$$
$$= P^{ext} \int_1^2 dV = P^{ext} (V_2 - V_1)$$

where we have taken P^{ext} outside the integral as it has a constant value.

If in a particular situation the gas pressure remains constant and is equal to the atmospheric pressure, we will have a reversible expansion at constant pressure. Suppose we take a liquid and confine it in a cylinder fitted with a piston. If the temperature of the liquid corresponds to it its normal boiling point, then the vapour pressure (1 atm) will be equal to the atmospheric pressure. As the volume of the system is increased, part of the liquid evaporates but the vapour pressure remains constant. In this case the expansion is reversible and it follows that

$$w_{rev} = \int_1^2 PdV = P(V_2 - V_1) \text{ where } P = P \text{ system } = P^{ext}$$

Isothermal reversible expansion of an ideal gas: If during expansion, a system does work on the surroundings, then the loss of the system energy causes its temperature to fall. To carry out an isothermal expansion, it is necessary to supply heat from outside to prevent a fall in temperature. This can be most easily done by connecting the system (temperature T) to a large heat reservoir at the same temperature.*

We now consider the special case of an isothermal reversible expansion of n moles of an ideal gas from V_1 to V_2. The relevant expression for the work is

$$w_{rev} = \int_1^2 PdV = \int_1^2 \frac{nRT}{V} dV = nRT \int_1^2 \frac{dV}{V} = nRT \ln \frac{V_2}{V_1}$$

where we have made use of the equation of state of ideal gas and the fact that temperature is constant.

For the two cases considered above, namely expansion at constant pressure and expansion under isothermal reversible conditions, the work obtained depends only on the initial and final states. This may seem to contradict our earlier statement that work is not a state function. There is, however, no contradiction once it is realised that in each of these special cases, there is only one unique path, consistent with the restrictions imposed, which connects the terminal states. For processes where multiple paths are available, work, in general, depends upon the path and it is not a state function. We shall now illustrate calculation of reversible and irreversible work.

Example 9.1 A litre of an ideal gas at 300 K and 10 atm pressure is held in a cylinder fitted with a frictionless piston. The gas is expanded isothermally to a final pressure of 1 atm in three different ways as follows:

(1) In process 1, the gas is expanded in one step against a constant opposing pressure of 1 atm [Fig. 9.5(a)]

(2) In process 2, the pressure is released in two steps, first to 5 atm, and then to 1 atm [Fig. 9.5(b)].

(3) In process 3, the pressure is released in nine steps, first to 9, then to 8, to 7, to 6, to 5, to 4, to 3, to 2 and finally to 1 atm [Fig. 9.5(c)].

*One may wonder that when the heat reservoir loses heat to the system during the expansion process, its temperature would fall. This difficulty is overcome by introducing an idealised heat reservoir which has infinite heat capacity. In practice, the reservoir can be made large enough so that the heat loss does not effect its temperature sensibly.
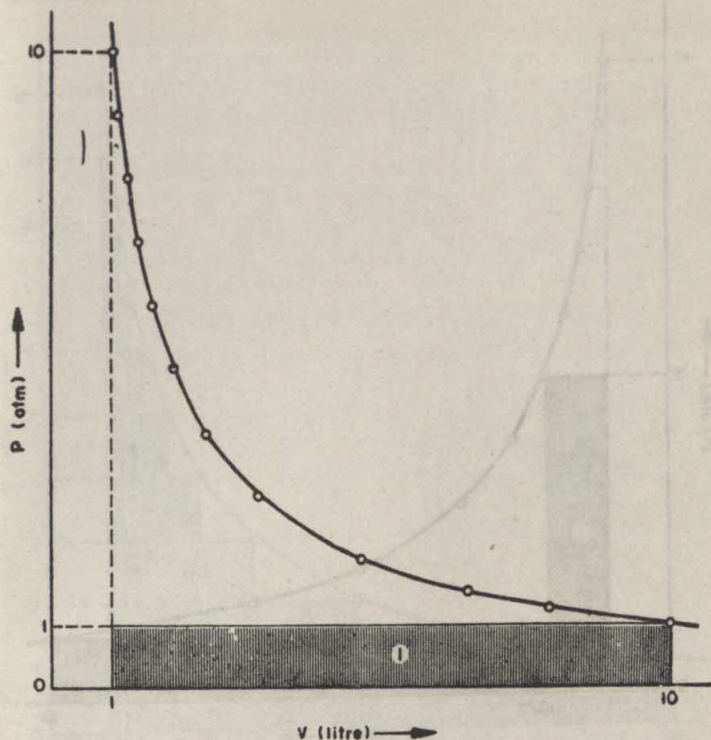
Fig. 9.5 (a) Work done in a one-step expansion process

Compute the work done by the gas during these irreversible isothermal expansions and compare these results with the work done in an isothermal reversible expansion from 10 atm to 1 atm at 300 K.

In process 1, the work done is

$$w = P^{ext} \, dV = 1 \times (10-1) = 9 \text{ litre atm}$$

In process 2, the work done

$$w = \text{WORK DONE IN STEP } 1 + \text{WORK DONE IN STEP } 2$$
$$= 5(2-1) + 1(10-2) = 5+8 = 13 \text{ litre atm}$$

In process 3, the work done is as shown below:

Step	Constant pressure against which the expansion is done, (P^{ext} in atm)	Change in volume involved (litre)	Work done $w = P^{ext} \Delta V$ (litre atm)
1	9	$\frac{10}{9} - 1$	1·00
2	8	$\frac{10}{8} - \frac{10}{9}$	1·11
3	7	$\frac{10}{7} - \frac{10}{8}$	1·25
4	6	$\frac{10}{6} - \frac{10}{7}$	1·43
5	5	$\frac{10}{5} - \frac{10}{6}$	1·67
6	4	$\frac{10}{4} - \frac{10}{5}$	2·00
7	3	$\frac{10}{3} - \frac{10}{4}$	2·50
8	2	$\frac{10}{2} - \frac{10}{3}$	3·33
9	1	$\frac{10}{1} - \frac{10}{2}$	5·00
WORK DONE IN TOTAL OF 9 STEPS			19·29
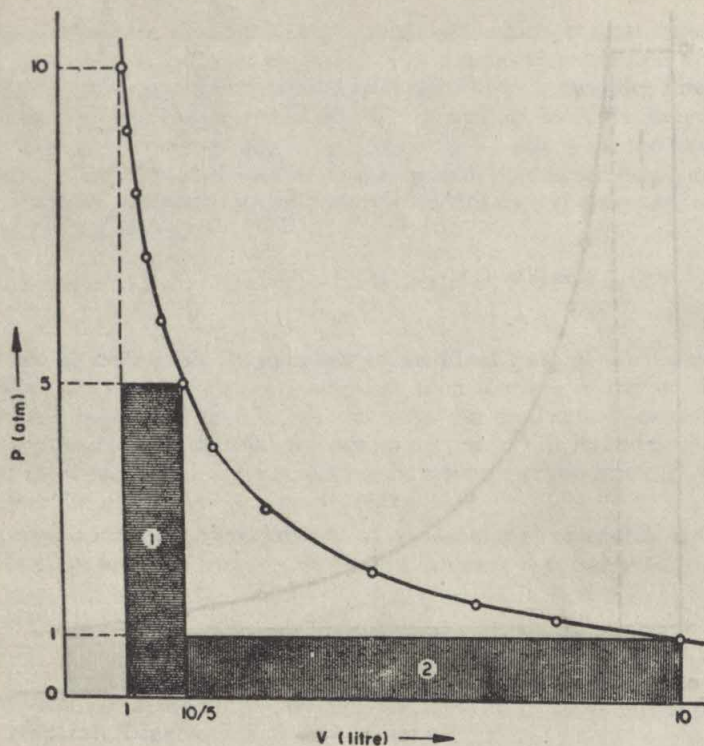
Fig. 9.5 (*b*) Work done in a two-step expansion process

Work done in isothermal reversible expansion, $w_{rev} = nRT \ln \dfrac{V_2}{V_1}$

Since $nRT = PV = 10$ litre atm, $V_2 = 10$ litres and $V_1 = 1$ litre, we have

$$W_{rev} = 10 \ln \tfrac{10}{1}$$
$$= 10 \times 2 \cdot 303 \log \tfrac{10}{1} = 23 \cdot 03 \text{ litre atm}$$

The work done in the nine-step expansion is more than in the two-step expansion which in turn is more than in the one-step expansion. If we carry out the expansion in still large number of steps, the work done by the system would be still larger and it can be made to approach the maximum attainable value of $23 \cdot 03$ litre-atm in the isothermal reversible process. The work has an upper limit of definite value only because the temperature is constant along the path. If the temperature were to change along the path, there would be no upper limit on the work produced by the system.

9.2.2 Heat

Heat is another mode by which a system can exchange energy with the surroundings. Whenever a system and its surroundings are not at the same temperature, heat either flows in or out of the system. The quantity of heat involved in a process depends upon the path, i.e. heat, like work, is not a state function. It follows therefore that to compute the heat evolved or absorbed, the details of the process must be known. Reversible transfer of heat between two bodies can be achieved by maintaining throughout an infinitesimal temperature dif-
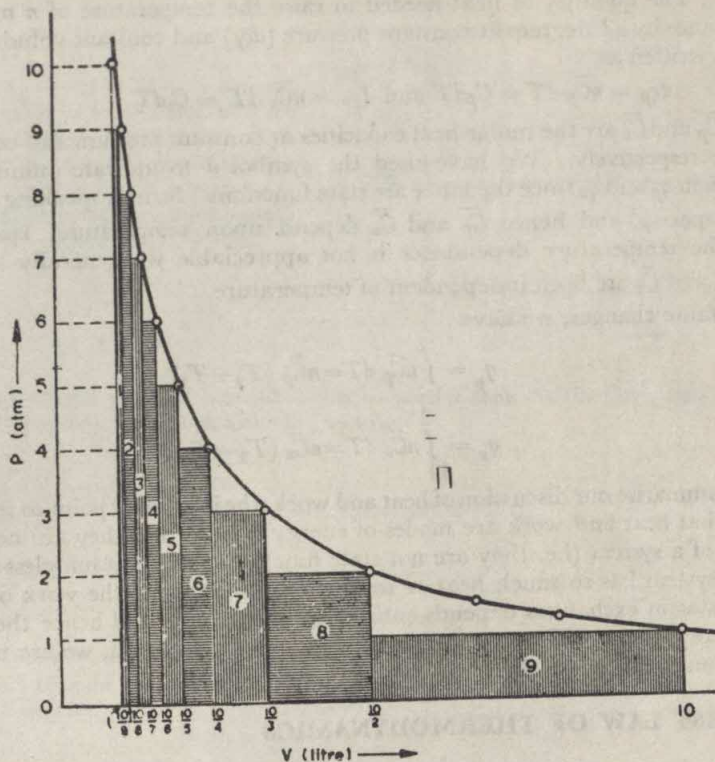
Fig. 9.5 (c) Work done in a nine-step expansion process

ference between the bodies (see the earlier discussion of reversible expansion). Heat, like work, is an extensive quantity.

We shall indicate small amount of heat as δq and finite amount by q. Further, the heat *added* to the system will be considered *positive* $(+q)$ while the heat *lost* by the system will be considered negative $(-q)$. It should be noted that this choice is opposite to that adopted in the case of work.

The amount of heat required to raise the temperature of 1 g of a substance by 1°C is called the *specific heat* of the substance. In chemical problems, the so-called *molar heat capacity* is a more useful quantity. It is defined as the amount of heat necessary to raise the temperature of one mole of a substance by 1°C. Molar heat capacity $(\overline{C})$ depends upon the nature of the substance. It is obviously an intensive quantity. The corresponding extensive quantity is known as heat capacity (C).

The amount of heat (δq) required to raise the temperature of n moles of a substance by dT degrees is

$$\delta q = n\overline{C}dT = CdT$$

This expression follows from the definition of $\overline{C}$ and C given above. The equation shows that molar heat capacity must also, in general, depend upon the path. However, under special conditions where a definite path is specified, heat and molar heat capacity can become state functions. Two processes which fall in this category are those carried out (*i*) at constant pressure and (*ii*) at constant

volume. The quantity of heat needed to raise the temperature of n moles of a substance by dT degrees at constant pressure (dq_p) and constant volume (dq_v) can be written as

$$dq_p = n\overline{C_p}\, dT = C_p dT \text{ and } dq_v = n\overline{C_v}\, dT = C_v dT$$

Here, $\overline{C_p}$ and $\overline{C_v}$ are the molar heat capacities at constant pressure and constant volume respectively. (We have used the symbol d to indicate infinitesimal changes in q_p and q_v since the latter are state functions.) Strictly speaking, molar heat capacity, and hence $\overline{C_p}$ and $\overline{C_v}$ depend upon temperature. However, since the temperature dependence is not appreciable we generally assume that $\overline{C_p}$ and $\overline{C_v}$ are both independent of temperature.

For finite changes, we have

$$q_p = \int_1^2 n\overline{C_p}\, dT = n\overline{C_p}\,(T_2 - T_1)$$

$$q_v = \int_1^2 n\overline{C_v}\, dT = n\overline{C_v}\,(T_2 - T_1)$$

To summarise our discussion of heat and work, the important point to remember is that heat and work are modes of energy transfer but they are not properties of a system (i.e. they are not state functions). It is meaningless to say that a system has so much heat or so much work, because the work or heat that a system exchanges depends entirely on the process and hence they will be different under different conditions. With this background, we are now in a position to formulate the first law of thermodynamics.

9.3 FIRST LAW OF THERMODYNAMICS

It has been shown in the previous section that q and w are path-dependent quantities. However, experience shows—and this is the essential content of the first law—that the difference $q-w$ is independent of the path and depends only upon the initial and final states of a system. The difference $q-w$ is commonly designated as ΔE and it is identified with the change in energy (E) of the system. The following equations represent different ways of stating the first law of thermodynamics mathematically:

$$\delta q - \delta w = dE$$
$$\text{or} \quad q - w = \Delta E$$

The fact that dE is independent of path means that E must be a state function. The first law can be, therefore, also stated as: *There exists an energy function, E, for every system that depends only upon the state of the system and it is independent of the way the system is brought to that state.*

Example 9.2 One mole of an ideal gas occupies 1 litre volume at 100 K (initial state) and two litre volume at 200 K (final state). The change from the initial to final state is brought about along the two paths ABC and ADC (Fig. 9.6). Calculate w, q and E for both the paths and show that q and w are path-dependent whereas ΔE is path-independent.

Path ADC: The gas is taken isothermally reversibly from A to D, therefore,

$$dw = R \times 100 \ln \tfrac{2}{1} = 100\, R \ln 2$$

In an isothermal reversible expansion of an ideal gas, the amount of heat extracted from a reservoir is converted into an equivalent amount of work, therefore $q = w$.

Fig. 9.6 Two paths *ABC* and *ADC* are shown connecting the states *A* and *C*. Note that this is a *T–V* plot. Hence the areas in the plots do not correspond to work. To obtain the work, it is necessary to plot the corresponding *P–V* data.
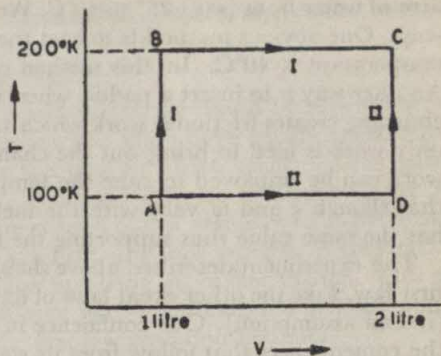
From *D* to *C*, the volume is constant so that no work is done. As the temperature changes from 100 K to 200 K, therefore, along *D* , we have

$$w = 0$$

$$q = \int_{100}^{200} \bar{C}_v \, dT = C_v(200-100) = 100 \, \bar{C}_v$$

Thus along path *ADC*,

$$w = 100 \, R \ln 2$$

$$q = 100 \, R \ln 2 + 100 \, \bar{C}_v$$

$$\text{and} \quad \Delta E = q - w = 100 \, \bar{C}_v$$

Path ABC: Here the gas is first heated up to temperature 200 K at constant volume, therefore along *AB* we have,

$$w = 0$$

$$q = \int_{100}^{200} \bar{C}_v \, dT = 100 \, \bar{C}_v$$

In taking the gas from *B* to *C*, the temperature remains constant, therefore, along *BC*, we have

$$q = w = R \times 200 \ln \tfrac{2}{1} = 200 \, R \ln 2$$

and along path *ABC*,

$$q = 200 \, R \ln 2 + 100 \, \bar{C}_v$$

$$w = 200 \, R \ln 2$$

$$\Delta E = q - w = 100 \, \bar{C}_v$$

For an isolated system, q and w are zero. The first law equation then implies that

$$(dE)_{\text{isolated system}} = 0$$

which means that the energy of an isolated system is constant. Since the universe by definition is an isolated system, the first law can be alternately stated as: *The energy of the universe is conserved. Inside the universe, energy can be transferred from one part to another, or it can be converted from one form to another, but it can neither be created nor destroyed.*

The last statement identifies the first law as the *law of conservation of energy* and this is perhaps the most popular version of this law.

We now discuss a simple experiment which supports the assertion that E is a state function. Consider the problem of raising the temperature of one

litre of water from (say) 25° to 40°C. We can effect this change in a number of
ways. One obvious method is to heat the water at 25°C over a burner until the
temperature is 40°C. In this method only heat is transferred to the system.
Another way is to insert a paddle wheel in the water and churn the wheel. The
churning creates frictional work which raises the temperature. In this method,
only work is used to bring out the change. Various combinations of heat and
work can be employed to raise the temperature by 15°C. Experiments shows
that though q and w vary with the method, the difference $q-w$ in each case
has the same value thus supporting the first law.

The experiment described above should not be regarded as a 'proof' of the
first law. Like the other great laws of nature, the first law is simply a postulate
(i.e. an assumption). Our confidence in this law stems from the fact that all
the consequences that follow from its statement are in perfect agreement with
experiments conducted so far.

The statement that energy is conserved also becomes imperative when we
explore nature from another viewpoint. One can argue that if conservation
of energy is *not* a universal law of nature, then it should be possible to create
energy. In other words, by clever designs one should be able to put less energy
into some machine and get more energy. And if energy can be created this
way, with less or zero input of energy, one may be able to build a perpetual
motion machine which runs continuously without requiring any driving agency.
Many have tried to evolve such a perpetual motion machine; however, all
such attempts have failed.* This experience also leads us to believe in the
validity of the first law.

It should be noted that the first law equation defines only *change* of energy
and not the energy itself. The absolute value of the energy of a system is of no
consequence in thermodynamics. As far as the first law is concerned, it is enough
to assert that a state function like energy exists. What this function means is
a question that thermodynamics is incapable of answering. To interpret E,
we need to step outside the domain of classical thermodynamics and make use
of atomic-molecular theory. The answer from the microscopic viewpoint is
very simple. The energy of a system is nothing more than the sum of kinetic
energy of atoms and molecules, potential energy of interaction between atoms
and molecules, and kinetic and potential energies of electrons and nuclei
constituting the atoms and molecules.

Before we move on to discuss the applications of the first law, it must be
pointed out that we have considered only two modes of energy transfer namely
heat and mechanical work. Several other modes like electrical work, magnetic
work and so on exist and the first law can be generalised to handle *all* modes of
energy transfer.

9.4 ENTHALPY

Let us explore further the first law equation

$$\delta q = dE + \delta w = dE + P^{ext}\, dV$$

where in the second equality we have written the presssure-volume work expli-

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*It may be mentioned here that in nuclear fission and fusion reactions, the energy that is
released comes from conversion of mass into energy in accordance with the equation $E=mc^2$.

citly. If in a particular process, the volume of a system is maintained constant (i.e. $dV=0$), then

$$dq_v=dE$$

This means that energy changes in a system can be found by measuring the heat exchanged in a constant volume process. The above equation also shows that q_v should be a state function—a fact that we stated earlier without proof.

The isochoric process is, however, of limited interest to chemists since the vast majority of chemical reactions are carried out in vessels open to the atmosphere, i.e. under conditions where pressure, and not volume, is constant. It is therefore, desirable to find a relation involving q_p, rather than q_v. This can be easily done in two steps. We first note that when external pressure equals the system pressure (i.e. $P^{ext}=P$), the first law equation becomes

$$dq_p=dE+PdV = d(E+PV)$$

where we have taken account of the fact that q_p is a state function. We next define a new state function, H, called *enthalpy* as

$$H=E+PV$$

from which it follows that

$$dH=dE+pdV+VdP$$

At constant pressure this reduces to

$$dH=dE+PdV+VdP$$

This shows that heat exchanged in a constant pressure process is equal to the change in enthalpy of the system. If the enthalpy change of a system is negative (i.e. the system loses heat), the process is called *exothermic* whereas if the enthalpy change is positive (i.e. the system absorbs heat), the process is known as *endothermic*.

Enthalpy may be regarded as a modified energy function which includes pressure-volume work. Because of its relation to heat exchanged at constant pressure, the enthalpy function, rather than the energy function, finds widespread use in chemical thermodynamics. It is obvious from the definition that enthalpy is an extensive quantity.

We have earlier defined molar heat capacities C_p and C_v as

$$C_p = dq_p/dT \quad \text{and} \quad C_v = dq_v/dT$$

The equivalence of dq_p with dH and of dq_v with dE permits us to write

$$C_p = (dH/dT)_p \quad \text{and} \quad C_v = (dE/dT)_v$$

The change in enthalpy of n moles of a substance with temperature is

$$\Delta H=\int_1^2 dH=n\int_1^2 \bar{C}_p dT$$

Assuming $\bar{C}_p$ to be independent of temperature, we get

$$\Delta H=n\bar{C}_p(T_2-T_1)$$

Similarly if $\bar{C}_v$ is assumed to be temperature independent, we get

$$\Delta E=n\bar{C}_v(T_2-T_1)$$

9.4.1 Kirchoff's Relation

We have earlier used the relation

$$dH=C_p dT$$

which shows the variation of enthalpy of a substance with temperature. Thus the change in enthalpy of a substance when the temperature is changed from T_1 to T_2 is

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

For a chemical reaction

$$aA + bB \rightarrow cC + dD$$
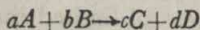
we may write the change in enthalpy as

$$\Delta H = H\,(\text{PRODUCTS}) - H\,(\text{REACTANTS})$$

and

$$\frac{d(\Delta H)}{dT} = \frac{dH\,(\text{PRODUCTS})}{dT} - \frac{dH\,(\text{REACTANTS})}{dT} \qquad (P = \text{CONST})$$

$$= C_p\,(\text{PRODUCTS}) - C_p\,(\text{REACTANTS})$$

or $d(\Delta H) = [C_p\,(\text{PRODUCTS}) - C_p\,(\text{REACTANTS})]\ dT$

$$= \Delta C_p dT$$

On integrating between the limits T_1 and T_2, we obtain

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p\ dT$$

or

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_p\ dT$$

where ΔH_2 and ΔH_1 are the enthalpy changes of the reaction at temperatures T_2 and T_1 respectively.

This relation, known as the *Kirchoff relation*, is useful for calculating the enthalpy change of a chemical reaction at any temperature if its value at some other temperature is known.

Example 9.3 For the reaction

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g) \quad \Delta H_{298} = -57.80 \text{ kcal}$$
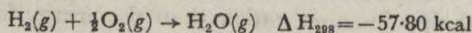
find ΔH at 398 K. The molar heat capacities $(\bar{C}_p)$ are: $H_2\,(g) = 6.9$; $O_2\,(g) = 7.0$ cal; $H_2O\,(g) = 8.0$ cal mol^{-1} deg^{-1}.

From Kirchoff's equation,

$$\Delta H_{398} = \Delta H_{298} + \int_{298}^{398} \Delta C_p dT$$

$$\Delta C_p = \underset{\text{PRODUCTS}}{\Sigma\ C_p} - \underset{\text{REACTANTS}}{\Sigma\ C_p}$$

$$= \bar{C}_p(H_2O) - [\bar{C}_p(H_2) + \tfrac{1}{2}\bar{C}_p(O_2)]$$

$$= 8.0 - [6.9 + \tfrac{1}{2}(7.0)] = -2.4 \text{ cal deg}^{-1}$$

and $\Delta H_{398} = -57,800 + (-2.4)\,(398 - 298)$

$$= -57,800 - 240 = -58.04 \text{ kcal}$$

Note that we have assumed that the difference in heat capacities, i.e. ΔC_p is independent of temperature.

9.5 IDEAL GAS CALCULATIONS

Before proceeding to apply the first law of thermodynamics to chemical reactions, it is useful to consider applications of this law to ideal gas behaviour as it helps to further clarify the various concepts developed so far.

9.5.1 Relation between ΔH and ΔE

There are situations where one of the two quantities ΔH and ΔE is known and the other has to be calculated. Such calculations are particularly simple for an ideal gas. From the definition of enthalpy $H = E + PV$ it follows that

$$\Delta H = \Delta E + \Delta (PV)$$

For n mol of an ideal gas

$$\Delta H = \Delta E + \Delta (nRT)$$

If the ideal gas forms a close system, n cannot change. Therefore,

$$\Delta H = \Delta E + nR\Delta T$$

For the special case of an isothermal process $(T=0)$, $\Delta H = \Delta E$.

Next consider a reaction

$$aA(g) + bB(g) = cC(g) + dD(g)$$
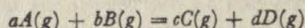
between ideal gases taking place at constant temperature T. Here the number of moles may change and the change Δn is given by*

$$\Delta n = (c+d) - (a+b)$$

If Δn is not zero, ΔH and ΔE will be different even though the temperature is constant. To find their relation, we go back to the starting equation $\Delta H = \Delta E + \Delta (PV)$ where

$$\Delta (PV) = (PV)_{\text{final state}} - (PV)_{\text{initial state}}$$

For the above mentioned reaction

$$(PV)_{\text{final state}} = (PV)_{\text{products}} = (c+d)RT$$

where the last equality follows from Dalton's law of partial pressures. Similarly

$$(PV)_{\text{initial state}} = (PV)_{\text{reactants}} = (a+b)RT$$

$$\therefore \Delta (PV) = [(c+d) - (a+b)]RT$$
$$= (\Delta n)RT$$

$$\text{or} \quad \Delta H = \Delta E + (\Delta n)RT$$

When substances other than ideal gases are involved, the relation between ΔH and ΔE is not as straightforward. However, a few general, but qualitatively, useful statements can be made in these cases. ΔH and ΔE differ appreciably only for processes involving gaseous substances. For solids and liquids, $(PV)_{\text{final}}$ is usually only slightly different from $(PV)_{\text{initial}}$. Hence ΔH and ΔE are nearly equal for changes in condensed phases.

9.5.2 Relation between $\bar{C}_P$ and $\bar{C}_V$

$$H = E + PV = E + RT \qquad \text{for one mol of an ideal gas}$$

$$\text{or} \quad \frac{dH}{dT} = \frac{dE}{dT} + \frac{d(RT)}{dT} = \frac{dE}{dT} + R$$

But $\dfrac{dH}{dT} = \bar{C}_P$ and $\dfrac{dE}{dT} = \bar{C}_V$, therefore,

$$\bar{C}_P - \bar{C}_V = R$$

This relation is valid only for (one mol of) ideal gases. For other gases, the relation gets more complicated, but $\bar{C}_P$ is always greater than $\bar{C}_V$. This is easily understandable since in a constant pressure process (but not in a constant volume process) a system has to do work against the surroundings. As such, more heat would be needed to effect a given temperature rise at constant pressure than at constant volume, i.e. $\bar{C}_P$ is larger than $\bar{C}_V$. In condensed phase, volume

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*Note that change in moles is defined as the total number of moles of the products *minus* the total number of moles of the reactant. If the former is less than the latter, Δn will be a negative number.

22

changes are small; therefore the work done at constant pressure is also small. It follows, therefore, that $\bar{C}_P$ and $\bar{C}_V$ are almost equal for solids and liquids.

9.5.3 Reversible Expansion at Constant Pressure

Let one mol of an ideal gas expand reversibly from the initial state (P, V_1, T_1) to the final state (P, V_2, T_2). The work done in this process, w_{rev} is (see section 9.2.1)

$$w_{rev} = P(V_2 - V_1) = R(T_2 - T_1)$$

Similarly, the heat absorbed, q_p, is given by

$$q_P = \bar{C}_P(T_2 - T_1)$$

But $\Delta H = q_p$, therefore, $\Delta H = \bar{C}_P(T_2 - T_1)$ and

$$\Delta E = q - w \text{ (from the first law)}$$
$$= \bar{C}_P(T_2 - T_1) - R(T_2 - T_1)$$
$$= (\bar{C}_V + R)(T_2 - T_1) - R(T_2 - T_1)$$
$$= \bar{C}_V(T_2 - T_1)$$

9.5.4 Reversible Process at Constant Volume

Since the process is carried out reversibly $P^{syst} = P^{ext}$ and $T^{syst} = T^{ext}$. Let the initial state of one mol of an ideal gas be (P_1, V, T_1) and the final state (P_2, V, T_2). If P_2 is less than P_1, then T_2 will also be less than T_1, i.e. if the pressure of the system is decreased keeping the volume constant then the temperature of the system will also fall implying that the system must lose heat.

The expressions for the various quantities are

$$w = 0$$
$$q_v = \int_{T_1}^{T_2} \bar{C}_v dT = \bar{C}_v(T_2 - T_1) = \Delta E$$

Since $T_2 < T_1$, q_v is a negative quantity, in agreement with the statement made above. The calculation of ΔH is now a simple matter.

$$\Delta H = \Delta E + \Delta(PV) = \Delta E + R\Delta T = \Delta E + R(T_2 - T_1)$$

But $\Delta E = \bar{C}_V(T_2 - T_1)$ Therefore,

$$\Delta H = \bar{C}_V(T_2 - T_1) + R(T_2 - T_1)$$
$$= (\bar{C}_V + R)(T_2 - T_1) = \bar{C}_P(T_2 - T_1)$$

9.5.5 Reversible Process at Constant Temperature

We consider the change of one mol of an ideal gas from the state (P_1, V_1, T) to (P_2, V_2, T). As we are interested in calculating changes in state functions like ΔE and ΔH, we can choose any path. For convenience, we shall carry out the process in the following manner.

$$(P_1, V_1, T) \rightarrow (P_2, V_1, T') \rightarrow (P_2, V_2, T)$$

In the first step, volume is held constant with the result that the temperature changes to some value T'; in the second step, pressure is kept constant such that volume changes to V_2 and temperature returns to its original value.

The first step corresponds to the constant volume process discussed in the preceding section. Making use of the results obtained there, we have,

$$w = 0, q_v = \bar{C}_V(T' - T)$$
$$\Delta E = \bar{C}_V(T' - T), \Delta H = \bar{C}_P(T' - T)$$

For the second step, we use the results of section 9.5.3.

$$w = R(T - T'), q_p = \bar{C}_P(T - T')$$
$$\Delta E = \bar{C}_V(T - T'), \Delta H = \bar{C}_P(T - T')$$

Adding the two contributions, the various quantities for the overall constant temperature process are

$$w = R(T - T'), \quad q = \bar{C}_P(T - T') + \bar{C}_V(T' - T)$$
$$= (\bar{C}_V + R)(T - T') + \bar{C}_V(T' - T)$$
$$= \bar{C}_V(T - T') + \bar{C}_V(T' - T) + R(T - T') = R(T - T')$$
$$\Delta E = \bar{C}_V(T - T') + \bar{C}_V(T' - T) = 0$$
$$\Delta H = \bar{C}_P(T' - T) + \bar{C}_P(T - T') = 0$$

The first law is obviously satisfied as can be seen from the values of q, w and ΔE.

In isothermal processes involving ideal gases, ΔH and ΔE are always zero. This is because enthalpy and energy of an ideal gas depend only on temperature and not on pressure or volume. Consequently, when either pressure or volume changes, with temperature remaining constant, enthalpy and energy of an ideal gas remain constant. Thermodynamics cannot and does not offer any interpretation of this behaviour. The kinetic viewpoint, however, readily explains this feature. We have seen in Chapter 6 that in an ideal gas there are no attractive forces between molecules. Consequently, energy is not needed to move molecules further apart (as in expansion); neither is energy released when molecules come together (as in contraction). Energy of an ideal gas is, thus, independent of its volume.

9.5.6 Reversible Isothermal Expansion

We can effect the change from (P_1, V_1, T) to (P_2, V_2, T) discussed above, along a reversible isothermal path where temperature is throughout constant. Since the initial and final states are the same as in section 9.5.5, ΔE and ΔH should both be zero:

$$\Delta E = \Delta H = 0$$

Since the path is different, q and w may be different. We have obtained earlier (section 9.2.1) the expression for w_{rev} in a reversible isothermal process. For one mol of an ideal gas it has the form, $w = RT \ln(V_2/V_1)$. Combining this with the first law we get, $q = RT \ln(V_2/V_1)$.

In an isothermal reversible expansion of an ideal gas, a certain amount of heat is extracted from the reservoir and converted into an equivalent amount of work, the energy of the system remaining unchanged.

9.6. HEAT OF REACTION

The heat change associated with a chemical reaction at a constant pressure and constant temperature is called the *heat of reaction*. The heat q_p and the enthalpy change ΔH are identical under these conditions, and the latter is generally used to represent heats of reaction. We are familiar with heats of reaction like heat of vapourisation, heat of sublimation and heat of fusion. Since heats of reaction vary depending on pressure and temperature, it is convenient to report heats of reaction in terms of *standard states of substances*.

The standard state of a substance is taken as the most stable form of the substance at 1 atm and 298 K. For example, since at 298 K and 1 atm pressure, graphite is more stable than diamond, graphite is taken as the standard state of solid carbon. The choice of the particular values of pressure and temperature in the definition of the standard state is, of course, entirely arbitrary.

When reactants and products are all in their standard states, the heat of reaction is written as $\Delta H°_T$, the subscript T referring to the temperature at which the reaction is carried out. Thus, for the combustion of methane in oxygen, we write,

$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(l) \quad \Delta H°_{298K} = -212 \cdot 8 \text{ kcal}$$
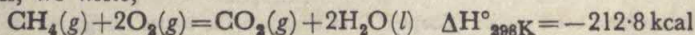
where $H_2O(l)$ refers to liquid water at 298 K. The $\Delta H°$ of this reaction will have a different value if water vapour is formed instead of liquid water. Heats

of reaction are usually measured by employing calorimeters. Since most chemical reactions are run at atmospheric pressure, tables of heats of reactions at 1 atm pressure and 298 K are usually available. When temperature and pressure values are not specifically given, it is understood that they refer to these standard conditions.

Like methane, graphite and diamond also burn in oxygen. The heat of combustion of graphite is $-94 \cdot 05$ kcal/mol.

$$C(graphite) + O_2(g) = CO_2(g) \quad \Delta H^{\circ}_{298K} = -94 \cdot 05 \text{ kcal}$$
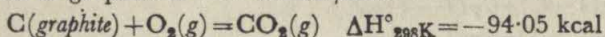
The heat of combustion of diamond, on the other hand, is $-94 \cdot 5$ kcal/mol.

$$C(diamond) + O_2(g) = CO_2(g) \quad \Delta H^{\circ}_{298}{}^{K} = -94 \cdot 5 \text{ kcal}$$
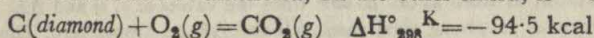
The difference in the heats of combustion of graphite and diamond is due to their enthalpy difference at 298 K. The heat of reaction in the hydrogenation of ethylene to form ethane is $-32 \cdot 8$ kcal/mol.

$$C_2H_4(g) + H_2(g) = C_2H_6(g) \quad \Delta H^{\circ}_{298K} = -32 \cdot 8 \text{ kcal}$$
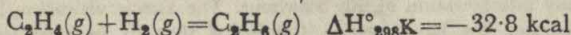
Formation of solid PCl_5 from liquid PCl_3 and gaseous chlorine is accompanied by evolution of $32 \cdot 8$ kcal/mol of heat:

$$PCl_3(l) + Cl_2(g) = PCl_5(s) \cdot \Delta H^{\circ}_{298K} = -32 \cdot 8 \text{ kcal}$$
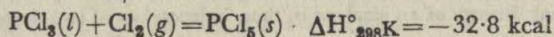
In order to focus our attention to an important aspect of heats of reaction let us follow the decomposition of methyl alcohol into its elements:

$$CH_3OH(l) + (3/2)O_2(g) = CO_2(g) + 2H_2O(l) \qquad \Delta H^{\circ}_{298K} = -173 \cdot 66 \text{ kcal}$$
$$2H_2O(l) = 2H_2(g) + O_2(g) \qquad \Delta H^{\circ}_{289K} = +136 \cdot 63 \text{ kcal}$$
$$CO_2(g) = C(graphite) + O_2(g) \qquad \Delta H^{\circ}_{298K} = + 94 \cdot 05 \text{ kcal}$$
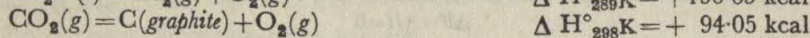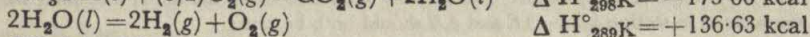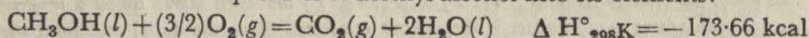
The overall reaction can be obtained by adding the above reactions:

$$CH_3OH(l) = C(graphite) + 2H_2(g) + \tfrac{1}{2}O_2(g)$$
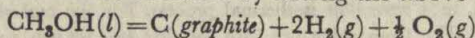
The overall enthalpy change can similarly be found out by the algebraic addition of the heats of reactions of the three reactions, and we get

$$\Delta H^{\circ}_{overall} = -173 \cdot 66 + 136 \cdot 63 + 94 \cdot 05 = +57 \cdot 02 \text{ kcal}$$

Since enthaply is a state function, the magnitude of enthalpy change is the same (i.e. is independent of the path) as long as the initial reactants and the final products are the same.

$$CH_3OH(l) \xrightarrow[\text{step}]{\text{one}} C(graphite) + 2H_2(g) + \tfrac{1}{2}O_2(g)$$

$$\downarrow +\tfrac{3}{2}O_2(g) \qquad \uparrow -O_2(g) \qquad \uparrow -\tfrac{1}{2}O_2(g)$$

$$\xrightarrow{\hspace{2cm}} CO_2(g) \ + \ 2H_2O(l)$$
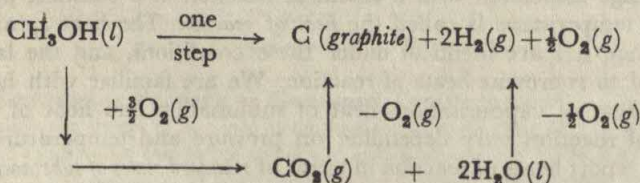
Thus, whether the decomposition of methyl alcohol takes place in three steps or in one step (as given in the overall reaction), ΔH° will be the same. This has a very important consequence. When the value of ΔH° in the one-step decomposition is unknown, it can be obtained by making use of the ΔH° values of other reactions as long as the overall reaction, when summed up turns out to be the same.* This important principle was recognised by Hess before the laws of thermodynamics were established. This principle whereby heats of reaction can be added or subtracted algebraically is called the *Hess law of*

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*This fact has been used earlier (Chapter 7) to compute the lattice energy via the Born-Haber cycle.

constant heat summation. It is good to recapitulate that the basis for this law is that at constant pressure, heat changes accompanying chemical reactions depend only on the initial and final states (and not on the path of the reaction).

9.7 HEATS OF FORMATION

The decomposition reaction of methyl alcohol considered earlier,

$$CH_2OH(l) = C(graphite + 2H_2(g) + \tfrac{1}{2}O_2(g) \quad \Delta H°_{298K} = 57·02 \text{ kcal}$$
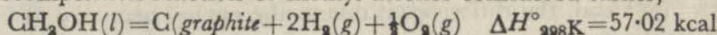
can be written in the reverse direction as

$$C(graphite) + 2H_2(g) + \tfrac{1}{2}O_2(g) = CH_2OH(l) \quad \Delta H°_{298K} = -57·02 \text{ kcal}$$
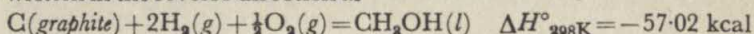
The latter reaction refers to the formation of methyl alcohol from the elements in their most stable form (standard states) at the specified temperature. Here, the heat of reaction $\Delta H°$ is the *heat of formation* of methyl alcohol. Similarly, every compound can be characterised with a definite heat of formation $\Delta H°_f$ which refers to the *enthalpy change associated with the formation of the compound from its elements*.

The heat of formation of ethyl alcohol is $-66·35$ kcal. That is, the reaction,

$$3H_2(g) + \tfrac{1}{2}O_2(g) + C(graphite) = C_2H_5OH(l)$$
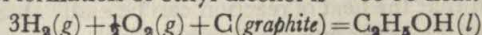
has a $\Delta H°_{298K}$ equal to $-66·35$ kcal. This is also written as

$$\Delta H°_{f298K} (C_2H_5OH, l) = -66·35 \text{ kcal}$$
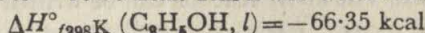
Similarly, $\Delta H°_{f298K}$ (H, g) $= 52·09$ kcal, $\Delta H°_{f298K}$ (CO$_2$, g) $= -94·05$ kcal, $\Delta H°_{f298K}$(HBr, g) $= -8·66$ kcal, $\Delta H°_{f298K}$ (n-Butane, g) $= -30·15$ kcal, and $\Delta H°_{f298K}$(o-Xylene, g) $= 4·54$ kcal, represent heats of formation of H (atomic hydrogen), CO$_2$, HBr, n-butane and o-xylene respectively at 298 K. The corresponding reactions are:
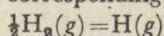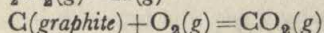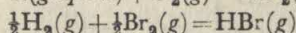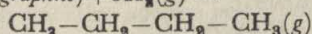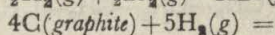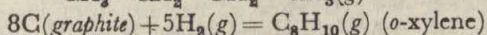
$$\tfrac{1}{2}H_2(g) = H(g) \qquad\qquad \Delta H°_{298K} = 52·089 \text{ kcal}$$
$$C(graphite) + O_2(g) = CO_2(g) \qquad \Delta H°_{298K} = -94·0518 \text{ kcal}$$
$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Br_2(g) = HBr(g) \qquad \Delta H°_{298K} = -8·66 \text{ kcal}$$
$$4C(graphite) + 5H_2(g) =$$
$$CH_3 - CH_2 - CH_2 - CH_3(g) \qquad \Delta H°_{298K} = -30·15 \text{ kcal}$$
$$8C(graphite) + 5H_2(g) = C_8H_{10}(g) \text{ (o-xylene)} \quad \Delta H°_{298K} = 4·540 \text{ kcal}$$

Heats of formation of compounds can either be obtained through direct experimental measurements of heats of reaction in which the compound of interest is formed from its elements, or, more commonly, by using available information on the heats of other reactions as shown in the previous section in the case of methyl alcohol. Heats of formation of some common substances are given in Table 9.1.

Table 9.1 Heats of Formation at 298 K in kcal/mol

H(g)	52·09	CO(g)	−26·41	C$_2$H$_6$(g)	−20·23
O(g)	59·16	CO$_2$(g)	−94·05	CH$_3$–CH$_2$–CH$_3$(g)	−24·82
Cl(g)	29·01	H$_2$O(g)	−57·80	CH$_3$–CH$_2$–CH$_2$–CH$_3$(g)	−30·15
Br(g))	26·71	H$_2$O(l)	−68·31	CH$_2$=CH$_2$(g)	12·96
I(g)	25·48	HF(g)	−64·2	CH$_3$–CH$_2$–OH	−56·625
N(g)	112·5	HCl(g)	−22·06	Benzene (g)	19·82
I$_2$(g)	14·87	HBr(g)	− 8·66	o-Xylene (g)	4·54
C(diamond)	0·45	HI (g)	6·20	m-Xylene (g)	4·12
NO (g)	21·60	CH$_4$ (g)	−17·89	p-Xylene (g)	4·29

By convention, heats of formation of elements are taken as zero if they refer to the most stable form of the substance at that temperature.

Thus, $\Delta H°_{f\,298K}(H_2, g) = 0$, $\Delta H°_{f\,298K}(N_2, g) = 0$, $\Delta H°_{f\,298K}(I_2, s) = 0$.
A less stable form of the substance at the same temperature, will have a positive value. For example: $\Delta H°_{f298K}(I_2, s) = 0$, but $\Delta H°_{f298K}(I_2, g) = 14\cdot87$ kcal, the difference of $14\cdot87$ kcal/mol is due to the heat of sublimation of iodine at this temperature. Similarly, $\Delta H°_{f298K}(H_2, g) = 0$, but $\Delta H°_{f298K}(H, g) = 52\cdot09$ kcal, the difference is due to the energy necessary to form one mol of atomic hydrogen from half a mol of molecular hydrogen.

9.7.1 Application of Heats of Formation Data

One important application of the data on heats of formation is to calculate heats of reaction in cases where experimental data are not available. Suppose we are interested in calculating the heat of combustion of *n*-butane at 298 K. The combustion reaction of *n*-butane can be written as

$$CH_3{-}CH_2{-}CH_2{-}CH_3(g) + (13/2)O_2(g) = 4CO_2(g) + 5\,H_2O(l)$$
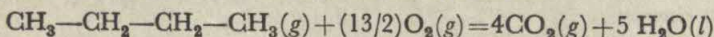
We have already seen that the heat of reaction can be easily obtained if we can break up the reaction of interest into component reactions for which the heats of reaction are known. The above reaction can be written as

$$CH_3{-}CH_2{-}CH_2{-}CH_3(g) = 4\,C(graphite) + 5\,H_2(g) \quad \Delta H°_1$$
$$4C(graphite) + 4O_2(g) = 4\,CO_2(g) \qquad\qquad\qquad \Delta H°_2$$
$$5H_2(g) + (5/2)\,O_2(g) = 5H_2O(l) \qquad\qquad\qquad \Delta H°_3$$
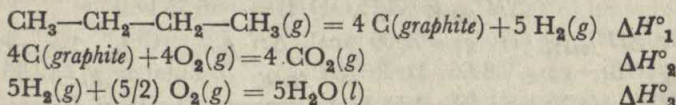
These reactions, when added up give the original reaction and the overall enthalpy change is, therefore, given by the algebraic addition of the three heats of reaction:

$$\Delta H°_{overall} = \Delta H°_1 + \Delta H°_2 + \Delta H°_3$$

We notice that $\Delta H°_1$ is the negative of $\Delta H°_f(CH_3{-}CH_2{-}CH_2{-}CH_3, g)$, and $\Delta H_3 = 5\Delta H°_f(H_2O, l)$. Hence we can write,
$$\Delta H°_{overall} = 4\Delta H°_f(CO_2, g) + 5\Delta H°_f(H_2O, l)$$
$$- \Delta H°_f(CH_3{-}CH_2{-}CH_2{-}CH_3, g)$$

This means that direct from the table of standard heats of formation the value of $\Delta H°_{overall}$ can be computed. From Table 9.1 $\Delta H°_f(CO_2, g) = -94\cdot05$, $\Delta H°_f(H_2O, l) = -68\cdot317$, and $\Delta H°_f(CH_3{-}CH_2{-}CH_2{-}CH_3, g) = -30\cdot15$ kcal/mol. Hence,

$$\Delta H°_{overall} = 4 \times (-94\cdot05) + 5 \times (-68\cdot31) - 30\cdot15 \text{ kcal} = -687\cdot79 \text{ kcal}$$

Since only heats of formation are involved in the calculation of $\Delta H°$, we can also directly compute the heat of reaction (without writing all the component chemical reactions whose heats of formation are used) as shown below:

$$CH_3{-}CH_2{-}CH_2{-}CH_3(g) + (13/2)O_2(g)$$
$$(\Delta H°_f = 30\cdot15) \qquad\qquad (\Delta H°_f = 0)$$
$$= \qquad 4CO_2(g) \qquad + \qquad 5\,H_2O(l)$$
$$(\Delta H°_f = 94\cdot05) \qquad (\Delta H°_f = -68\cdot31)$$
$$\Delta H° = 4\Delta H°_f(CO_2, g) + 5\Delta H°_f(H_2O, l)$$
$$- \Delta H°_f(CH_3{-}CH_2{-}CH_2{-}CH_3, g) - (13/2)\Delta H°_f(O_2, g)$$

As further examples, we calculate the heats of reaction of the following systems:

$$\frac{1}{2} H_2(g) \quad + \quad \frac{1}{2} Hg_2Cl_2(s) \quad = \quad Hg(l) \quad + \quad HCl(g)$$
$$(\Delta H°_f = 0) \quad (\Delta H°_f = -63\cdot32) \quad (\Delta H°_f = 0) \quad (\Delta H°_f = -22\cdot06)$$
$$\Delta H° = (-22\cdot06) - \frac{1}{2}(-66\cdot32) = 9\cdot60 \text{ kcal, and}$$

$$NaOH(s) \quad + \quad HCl(g) \quad = \quad NaCl(s) \quad + \quad H_2O(l)$$
$$(\Delta H°_f = -102\cdot0) \quad (\Delta H°_f = -22\cdot06) \quad (\Delta H°_f = -98\cdot32) \quad (\Delta H°_f = -68\cdot32)$$
$$\Delta H° = (-68\cdot32 - 98\cdot32) - (-102\cdot0 - 22\cdot06)$$
$$= -68\cdot32 - 98\cdot32 + 102\cdot0 + 22\cdot06 = 42\cdot58 \text{ kcal.}$$
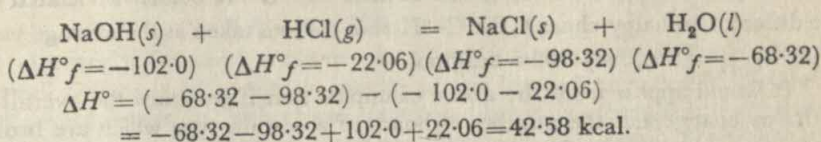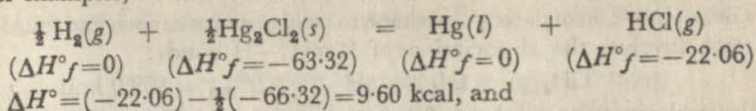
Example 9.4: Calculate the values of ΔH and ΔE at 25°C for the reaction:
$$F_2O(g) + H_2O(g) \rightarrow O_2(g) + 2 \, HF(g)$$
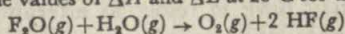
The standard heats of formation are $F_2O(g)$, 5·5 kcal mol^{-1}; $H_2O(g)$, $-57\cdot8$ kcal mol^{-1} and $HF(g)$, $-64\cdot2$ kcal mol^{-1}.

$$\Delta H = 2\Delta H°_f(HF) - [\Delta H°_f(F_2O) + \Delta H°_f(H_2O)]$$
$$= 2(-64\cdot2) - [(5\cdot5) + (-57\cdot8)] = -128\cdot4 + 52\cdot3 = -76\cdot1 \text{ kcal}$$

We know that $\Delta H = \Delta E + \Delta(PV) = \Delta E + \Delta(nRT)$ if the gases are assumed to behave ideally
or, $\quad \Delta E = \Delta H - \Delta nRT$ (since R and T are constants and n is the only variable)

$$= -76\cdot1 - 1 \times 1\cdot99 \times 298 = -76\cdot7 \text{ kcal}$$

NOTE: The internal energy decreases by 76·7 kcal but at 1 atm pressure only 76·1 kcal are given out as heat ($\Delta H = -76\cdot1$ kcal), the rest is used for work of expansion against 1 atm.

9.8 BOND ENERGIES

We have discussed how the heat or enthalpy change of a reaction can be calculated if the heats of formation of all the reactants and products are known. Often one needs to know the magnitude of such changes where heats of formation of participating species are unknown. Although exact predictions cannot be made, estimates can be worked out by using the information available on other compounds. One such method uses the concept of *bond energy* (see also Chapter 4).

Energy of a chemical bond between two atoms A and B, is the enthalpy change involved in the dissociation of the bond. In molecules involving more than one bond of the same type one takes an average value. We shall illustrate this with the help of the two O—H bonds of water; the enthalpy changes involved in successively breaking these two bonds in the vapour phase are:

$$\begin{array}{llll} H_2O(g) & = H(g) & + OH(g) & \Delta H°_{298} = 119\cdot95 \text{ kcal} \\ OH(g) & = H(g) & + O(g) & \Delta H°_{298} = 101\cdot19 \text{ kcal} \\ \hline H_2O(g) & = 2H(g) & + O(g) & \Delta H°_{298} = 221\cdot14 \text{ kcal} \end{array}$$
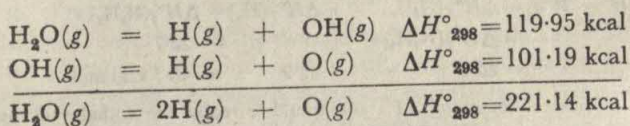
The enthalpy change involved in the rupture of first OH bond is significantly greater than breaking the second one; the average of these two values is taken as the bond energy of OH, i.e. $\epsilon_{O-H} = (1/2) \, (119\cdot95 + 101\cdot19) = 110\cdot57$ kcal/mol.

Decomposition of gaseous methane to yield gaseous carbon and four hydrogen atoms involves the dissociation of four C—H bonds:

$$CH_4(g) = C(g) + 4H(g) \quad \Delta H°_{298} = 398 \cdot 0 \text{ kcal}$$
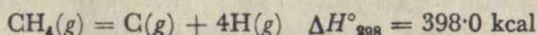
Although successive breaking of each of these four C—H bonds is associated with a different enthalpy change, the C—H *bond energy* is taken as the average value, i.e. $\epsilon_{C-H} = (1/4)(398) = 99 \cdot 5$ kcal/mol.

It would appear from the above examples that if we know the overall enthalpy change and the number of bonds of a certain type which are broken, we can calculate the bond energy. However, information on experimental enthalpy changes for reactions (as for the dissociation of CH_4) may not always be available, and one may have to resort to alternative methods. For this purpose, heats of combustion and dissociation energies of other simple molecules are often helpful. For example, the value of the enthalpy change in the dissociation of CH_4 can be computed using the $\Delta H°$ values of the following reactions which are experimentally known.

C(*graphite*)	$= C(g)$	$\Delta H° =$	171·69	kcal
$2H_2(g)$	$= 4H(g)$	$\Delta H° =$	208·36	kcal
$2H_2O(l)$	$= 2H_2(g) + O_2(g)$	$\Delta H° =$	136·6	kcal
$CO_2(g)$	$= C(graphite) + O_2(g)$	$\Delta H° =$	94·0	kcal
$CH_4(g) + 2 O_2(g)$	$= CO_2(g) + 2H_2O(l)$	$\Delta H° = -212 \cdot 8$		kcal

Adding, $CH_4(g) \quad = C(g) + 4H(g)$ $\Delta H° = 398 \cdot 0$ kcal
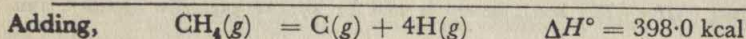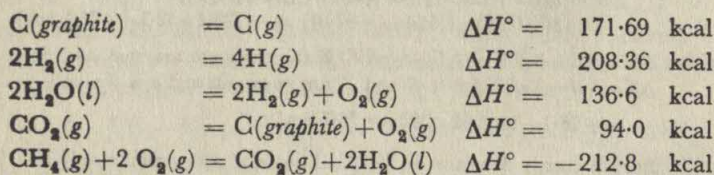
Once the bond energies of some bonds are known, those for many others can **be obtained** by using the known ones and additional thermochemical data.

We will now calculate $\epsilon_{N=N}$, the bond energy of a nitrogen–nitrogen double bond. From combustion data on NH_3, ϵ_{N-H} has been found to be 93·4 kcal/mol. Bond dissociation energy of N_2, $\epsilon_{N\equiv N}$, is 225·8 kcal/mol and that of H_2, ϵ_{H-H}, is 104·18 kcal/mol. From experiments it is possible to get a value for the $\Delta H°$ of the following reaction:

$$N_2H_4(g) = N_2H_2(g) + H_2(g) \quad \Delta H° = 26 \text{ kcal}$$
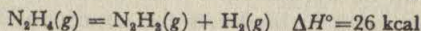
$\Delta H°_f$ for $N_2H_4(g)$ is 22·7 kcal/mol. If we take the structure of N_2H_2 to be H—N=N—H, with the help of the data given above we can readily calculate the bond energy of the double bond between the two nitrogen atoms, $\epsilon_{N=N}$. For this purpose, we shall first obtain the $\Delta H°_f$ value of N_2H_2 as follows:

$$N_2H_4(g) \quad = \quad N_2H_2(g) \quad + \quad H_2(g) \quad \quad \Delta H° = 26 \cdot 0 \text{ kcal}$$
$$\Delta H°_f = 22 \cdot 7 \quad \Delta H°_f(N_2H_2) = ? \quad \Delta H°_f = 0$$
$$\Delta H° = 26 \cdot 0 = \Delta H°_f(N_2H_2) \quad + \Delta H°_f(H_2) - \Delta H°_f(N_2H_4)$$
$$= \Delta H°_f(N_2H_2) \quad + 0 \quad - 22 \cdot 7$$
$$\text{or } \Delta H°_f(N_2H_2) \quad = 26 \cdot 0 \quad + 22 \cdot 7 \quad = 48 \cdot 7 \text{ kcal/mol}$$
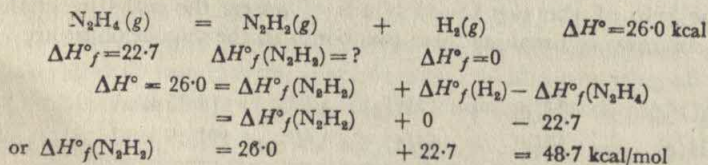
We know that the heat of formation of a compound is really the enthalpy change of that reaction in which the compound is formed from its elements. This means that $\Delta H°_f(N_2H_2)$ represents the $\Delta H°$ value of the following reaction:

$$N_2(g) + H_2(g) = N_2H_2(g) \quad \Delta H° = \Delta H_f°(N_2H_2) = 48 \cdot 7 \text{ kcal/mol}$$
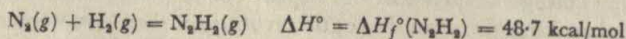
In this reaction, a triple bond of N_2 and a single bond of H_2 are broken, two N—H bonds and one N=N bond are formed. Bond breaking reactions require energy and the bond

making ones liberate energy, and the net difference shows up as the $\Delta H°$ of the reaction (48·7 kcal).

$$\Delta H° = 48·7 = \epsilon_{N \equiv N} + \epsilon_{H-H} - 2\epsilon_{N-H} - \epsilon_{N=N}$$
$$= 229·8 + 104·18 - 2 \times 93·4 - \epsilon_{N=N}$$

or $\epsilon_{N=N} = 94·48$ kcal/mol

Bond energies for various bonds were given in Chapter 4 (see Table 4.14). We shall note once again that *in actuality* similar bonds in a molecule, say the three N—H bonds in NH_3, have different dissociation energies; the bond energy in this case is only an average value for a N–H bond. This value is an approximation to the actual dissociation energy of the bond in any molecule.

We shall now illustrate the usefulness of bond energy values in estimating the heats of formation, taking the example of ethyl alcohol. We can write the reaction of carbon, hydrogen, and oxygen to produce ethyl alcohol vapour as follows:

$$2C \text{ (}graphite\text{)} + 3H_2(g) + \tfrac{1}{2}O_2(g) = \underset{\substack{| \quad |\\ H \quad H}}{\overset{\substack{H \quad H\\ | \quad |}}{H-C-C-O-H}}(g)$$
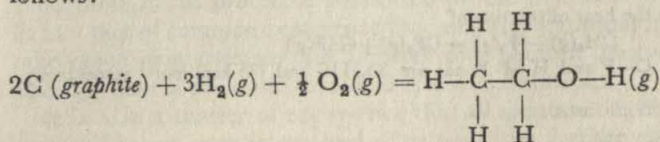
$$\Delta H° = \Delta H°_f (C_2H_5OHg)$$

Since in this reaction, ethyl alcohol vapour is formed from its elements, the heat of reaction is also the heat of formation of ethyl alcohol vapour. We can now relate the value of $\Delta H°_f(C_2H_5OH,g)$ to the bond energy in the following manner:

$$\Delta H°_f(C_2H_5OH)_g = \Delta H° = (2\Delta H°_{vap}(C) + 3\epsilon_{H-H} + \tfrac{1}{2}\epsilon_{O=O})$$
$$- (\epsilon_{C-C} + 5\epsilon_{C-H} + \epsilon_{C-O} + \epsilon_{O-H})$$

The heat of sublimation of carbon (the enthalpy change associated with transformation of graphite into carbon vapour) is 171·7 kcal/mol. Substituting the bond energy values we get,

$$\Delta H°_f(C_2H_5OH)_g = (2 \times 171·7) + (3 \times 104·2) + 1/2 \times 119)$$
$$- [83 + (5 \times 99) + 85 + 111]$$
$$= -58·5 \text{ kcal/mol}$$

This value of the heat of formation of ethyl alcohol vapour is an estimate from bond energy values. The experimental value for this quantity is $-56·625$ kcal/mol (Table 9·1). Thus, we see that although bond energy values are only average values, they are quite useful in predicting heats of formation and hence heats of reaction.

Some caution is necessary in the use of these estimated values of bond energies. We should remember that bond energy values are obtained in terms of some specific bonds in specific molecules, and finer variations in the enthalpy values for similar bonds present in other molecules cannot be exactly predicted. In some instances, depending on the structure of the molecule under consideration, the estimated value may be quite off the mark. One such case is found in the conjugated double bonds of benzene. The structure of benzene is as shown in (I).

Heat of formation calculated in terms of bond energies should be

$$\Delta H^\circ{}_f(C_6H_6)_g = 6\Delta H^\circ{}_{vap}(C) + 3\epsilon_{H-H} - 3\epsilon_{C=C} - 3\epsilon_{C-C} - 6\epsilon_{C-H}$$
$$= 65.4 \text{ kcal/mol}$$

(I)   (II)   (III)   (IV)   (V)   (VI)
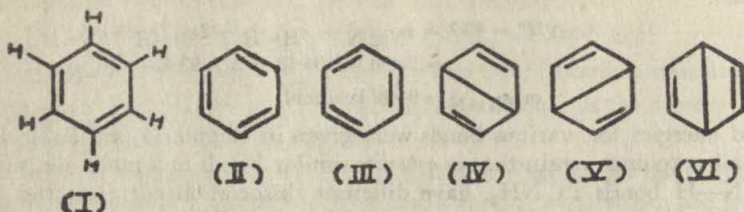
The experimental value, however, is only 19·82 kcal/mol. The difference, 45·58 kcal/mol, is ascribed to the additional stability of the molecule due to resonance between the structures II to VI (see Chapter 4 for a discussion of resonance phenomena).

Example 9.5 Calculate the heat of reaction of
$$CH_4(g) + 4F_2(g) \rightarrow CF_4(g) + 4HF(g)$$
Bond energies of F—F, C—F and H—F bonds are 38, 116 and 135 kcal mol^{-1} respectively.

This reaction involves:

(i) breaking of four C—H bonds
$$CH_4 \rightarrow 4C + 4H \quad \Delta H = 4(99.3) \text{ kcal}$$

(ii) breaking of four F—F bonds
$$4F-F \rightarrow 8F \quad \Delta H = 4(38) \text{ kcal}$$

(iii) Formation of four C—F bonds
$$C + 4F \rightarrow CF_4 \quad \Delta H = -4(116) \text{ kcal}$$

(iv) Formation of four H—F bonds
$$4H + 4F \rightarrow 4HF \quad \Delta H = -4(135) \text{ kcal}$$

The value of ΔH of the reaction is —454·8 kcal per mole of CF_4.

Example 9.6 For the reaction, $F_2O(g) + H_2O(g) \rightarrow O_2(g) + 2HF(g)$, calculate the ΔH of the reaction using average bond energies. Bond energies of O—F, O—H, H—F and O=O bonds are 44, 111, 135 and 119 kcal mol^{-1} respectively.

$$F-O-F\ (g) \rightarrow 2F(g) + O(g) \qquad \Delta H = 88 \text{ kcal}$$
$$H-O-H(g) \rightarrow 2H(g) + O(g) \qquad \Delta H = 222 \text{ kcal}$$
$$2O(g) \rightarrow O_2(g) \qquad \Delta H = -119 \text{ kcal}$$
$$2H(g) + 2F(g) \rightarrow 2H-F\ (g) \qquad \Delta H = -270 \text{ kcal}$$
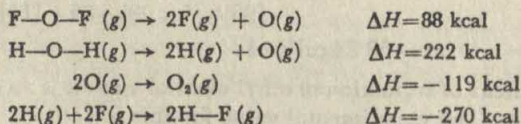
The sum of these gives, $\Delta H = -79$ kcal.

9.9 THE SECOND LAW OF THERMODYNAMICS

The first law rules out all changes in which the energy of the universe is not conserved. The first law does not, however, require that all transformations which conserve energy must necessarily take place. Indeed, several processes which are consistent with the energy conservation principle do not occur. Let us consider some familiar examples to illustrate this point.

Suppose we keep a cup of hot coffee in a room. It is a common observation that in the course of time coffee cools down by losing heat to the surroundings.

The energy of the universe is conserved in this process since the energy lost by the cup of hot coffee is gained by the surroundings. The reverse process in which a cup of coffee at room temperature warms *on its own* by absorbing heat from the surroundings would also be consistent with the first law, but this has never been observed.

As another example, consider a closed bottle of ammonia kept in one corner of a room. When the bottle is opened, the smell spreads in all directions, showing that ammonia has dispersed in the room. The reverse process, in which the dispersed ammonia in the room spontaneously accumulates in the open bottle has never been observed although such an occurrence would not violate the first law.

Our final example refers to the neutralisation of hydrochloric acid by sodium hydroxide. As soon as the solutions are mixed, heat is evolved with the formation of sodium chloride and water. But a solution of sodium chloride in water does not absorb heat on its own and yield the acid and the alkali even though this process is permitted by the first law. Such examples highlight a fact of common experience that all transformations in the universe which take place spontaneously (i.e. on their own without intervention of an outside agency) have a preferred and characteristic direction.

It is also a matter of experience that all spontaneous changes proceed until an equilibrium state is reached after which no further change takes place in the absence of external disturbances. For instance, in the examples discussed above, the coffee cools down until it is in thermal equilibrium with the surroundings; ammonia spreads until a uniform (equilibrium) distribution is achieved; and the neutralisation reaction stops for a certain well defined (relative) concentration of the reactants and products. These twin aspects of natural phenomena—namely that spontaneous processes have a characteristic direction and they eventually reach equilibrium—are completely unintelligible on the basis of the thermodynamic principles developed so far. We shall now show how the second law removes this deficiency.

It is convenient to begin by stating the second law; an understanding of the law can then be developed by applying it to some familiar situations. We emphasise that the second law is considerably more subtle than the first and proper appreciation of it comes only by applying it to diverse situations.

As in the case of the first law, there are several alternate but equivalent ways of stating the second law. Perhaps the most useful statement for chemical applications is: *There exists a function ' S ', called entropy, which is a state function. The entropy of the universe remains constant in a reversible process but it increases in an irreversible process. The entropy of the universe never decreases.*

The *entropy function* introduced in the second law is defined as follows. If a system is taken from state 1 to state 2, then the entropy change (ΔS) of the system is given by

$$\Delta S = \int_{1}^{2} \frac{\delta q_{rev}}{T}$$

The point to note about this equation is that the equality is valid *only if the process connecting the states 1 and 2 is reversible*. This does not mean that ΔS is path-dependent. What this means is that although entropy is a state function (and therefore ΔS is path-independent), it can be computed from heat data

via the above equation *only if the heat data refers to a reversible path*. It follows that if we wish to calculate ΔS between two states connected by an irreversible process, then we *must* construct a *reversible path* between the two states, and use the heat change for *this path* in the above equation. Once we have obtained the value of ΔS, the same value holds for all the other paths (including irreversible paths) since S is a state function.

For some special processes, the above equation takes the forms

$$\Delta S = \frac{1}{T} \int_1^2 \delta q_{\text{rev}} \qquad \text{(isothermal process)}$$

$$\Delta S = \frac{1}{T} \int_1^2 dq_{p,\text{rev}} = \frac{\Delta H}{T} \qquad \text{(isothermal, isobaric process)}$$

$$\Delta S = \frac{1}{T} \int_1^2 dq_{v,\text{rev}} = \frac{\Delta E}{T} \qquad \text{(isothermal, isochoric process)}$$

The usefulness of the second law for predicting the direction of natural processes and their eventual approach to equilibrium state, arises in the following manner. The term ' natural process ' means that the process is spontaneous, i.e. the process does not have to be induced from outside but takes place on its own. In this sense, the three examples considered at the beginning of this section are examples of natural processes.* Now every natural (spontaneous) process is necessarily irreversible, because during the process the system is not in equilibrium. This irreversible nature of spontaneous processes immediately establishes the connection between the direction of the process and the second law in the form given above. To answer the question whether a particular process is spontaneous or not, all that we have to do is to compute the entropy change of the system and the surroundings for the stipulated process. If this change is positive, i.e. the entropy of the universe increases, then the process will take place spontaneously and irreversibly. To answer why the spontaneous change eventually ceases, we should compute the entropy change at every stage of the process. As long as the change is positive, the process will continue but if at some stage the change becomes zero, the process will stop and equilibrium will be established. On the other hand, if the entropy change of the universe is zero or negative, for any conceivable transformation of a system, then the system will be unable to change its state spontaneously and hence it must be at equilibrium.

There are two aspects of the second law which must be clearly understood. Firstly, the decision about spontaneity of a process can be only based on the entropy change of the universe and *not* on entropy change of either the system or the sorroundings alone. We shall meet some examples later, where for a natural process the entropy of the system decreases but this is entirely

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*Natural process does not mean that the reverse process cannot take place, it only means that the reverse process has to be ' driven ' by an outside agency. For example, the flow of heat from higher to lower temperature is a natural process but heat *can be made* to flow from lower to higher temperature. This happens in the case of a refrigerator where heat flows from inside (lower temperature) to outside (higher temperature). But such an ' uphill ' flow of heat is possible only because the motor of a refrigerator acts as the ' driving ' agency.

permissible provided the entropy of the surroundings increases by even a larger amount. Secondly, the term 'spontaneous' contains no implication about the time element of the process. Examples are known where a spontaneous change in the thermodynamic sense does not take place, or takes place imperceptibly, because the rate of the permitted process is zero or negligibly small.

9.10 ENTROPY AND SPONTANEITY

We know from experience that when the external pressure is less than the internal pressure, a gas expands spontaneously. Similarly, when a hot body is in contact with a cold body, heat flows spontaneously from higher to lower temperature. Let us now see how the entropy criterion can be used to account for the spontaneity of these familiar processes.

9.10.1 Irreversible Isothermal Expansion

We first consider the special case of an ideal gas and, for simplicity, we restrict the discussion to expansion taking place under isothermal conditions.

Let one mole of an ideal gas expand in vacuum from an initial volume V_1 to a final volume V_2. Such an expansion can be easily carried out by taking a vessel of volume V_1 and connecting it to another evacuated vessel such that the total volume is V_2.

Since this irreversible expansion takes place against zero external pressure, $w_{irr} = 0$. Further since the process is isothermal and the substance is an ideal gas, $\Delta E = 0$. It therefore follows from the first law that $q_{irr} = 0$. However, we cannot use this value of q to calculate the entropy change of the system, since the latter must be computed from heat exchanged for a reversible path. We therefore devise a reversible process connecting the initial and the final states. Reversible isothermal expansion of one mol of an ideal gas has already been considered (section 9.2.1) and the results are $w_{rev} = RT \ln (V_2/V_1)$, $\Delta E = 0$.

$$\therefore q_{rev} = RT \ln (V_2/V_1)$$

The entropy change (ΔS) of the system $= q_{rev}/T = R \ln (V_2/V_1)$

This change depends only on the initial and the final states and not on the path. Hence even for the irreversible process, $(\Delta S)_{syst} = R \ln (V_2/V_1)$.

We next consider the entropy change of the heat reservoir which is at temperature T and which maintains the system at the same temperature. The heat reservoir is the only part of the surroundings that interacts with the system. Hence entropy change of the reservoir is also the entropy change of the surroundings.

In computing the value of ΔS of the reservoir, the only information one needs is whether the reservoir exchanges heat with the system or not. Since the system and the reservoir are at the same temperature, the exchange can be always carried out in a reversible manner. Therefore, the knowledge of heat transferred by the, or to the reservoir, is sufficient to calculate its entropy change. Now in the case of irreversible expansion in vacuum, w and ΔE are both zero; hence q is also zero. In other words during irreversible expansion against zero external pressure, the reservoir exchanges no heat. Therefore, $(\Delta S)_{surr} = q_{surr}/T = 0$. It follows that the entropy change of the universe is $(\Delta S)_{universe} = (\Delta S)_{syst} + (\Delta S)_{surr} = R \ln V_2/V_1$.

Since $V_2 > V_1$, ΔS of the universe is positive which means that irreversible expansion in vacuum must be a spontaneous process as indeed it is.

The above conclusion is not restricted to the free expansion of an ideal gas, but also applies to the isothermal irreversible expansion of a substance. We know that work obtained in a reversible expansion is maximum:

$$w_{rev} > w_{irr}$$

where w_{irr} is the work obtained in the corresponding irreversible process. (The inequality holds whether the irreversible expansion is carried out against zero external pressure or against some finite constant P^{ext} or against some finite changing P^{ext}.) We now rewrite the first law equation as follows:

$$w_{rev} = \Delta E + q_{rev}$$
$$w_{irr} = \Delta E + q_{irr}$$

These two relations correctly assure that w and q are different for reversible and irreversible processes although ΔE would be the same. Subtracting the two equations, we get

$$w_{rev} - w_{irr} = q_{rev} - q_{irr}$$

Since $w_{rev} > w_{irr}$, it follows that $q_{rev} > q_{irr}$. Now the entropy change of the system is given by

$$(\Delta S)_{syst} = q_{rev}/T$$

while that of the surroundings is given by

$$(\Delta S)_{surr} = - q_{irr}/T$$

The last equation may seem to contradict the requirement that entropy change must be calculated from a reversible process. No such contradiction is however involved since the subscript 'irr' refers to the process in which the *system* participates. The process in which the surroundings are involved (namely, the transference of heat) can always be done reversibly. Hence, the above equation correctly describes the entropy change of the surroundings. Combining the two equations, we get

$$(\Delta S)_{universe} = (\Delta S)_{syst} + (\Delta S)_{surr} = \frac{q_{rev}}{T} - \frac{q_{irr}}{T} > 0$$

thereby showing that the isothermal irreversible expansion is a spontaneous process.

9.10.2 Reversible Isothermal Expansion

This presents no problem since the system absorbs q_{rev}, and the surroundings lose $-q_{rev}$ amount of heat. Therefore,

$$(\Delta S)_{syst} = \frac{q_{rev}}{T}; \quad (\Delta S)_{surr} = - \frac{q_{rev}}{T} \text{ or } (\Delta S)_{universe} = 0$$

This is in agreement with the fact that a reversible isothermal expansion is not a spontaneous process and that every stage of such a process is an equilibrium stage.

9.10.3 Heat Flow from Higher to Lower Temperature

In order to apply the entropy criterion to a situation where temperature is not uniform we need to know the dependence of entropy on temperature. This

is easily done for constant pressure and for constant volume processes. We recall that

$$dS = \frac{dq_{P,\text{rev}}}{T} \qquad \text{(CONSTANT PRESSURE)}$$

$$\text{and } dS = \frac{dq_{v,\text{rev}}}{T} \qquad \text{(CONSTANT VOLUME)}$$

But $dq_P = n\bar{C}_P dT$ and $dq_v = n\bar{C}_V dT$

$$\therefore \quad dS = n\bar{C}_P dT/T \qquad \text{(CONSTANT PRESSURE)}$$

$$\text{and } dS = n\bar{C}_V dT/T \qquad \text{(CONSTANT VOLUME)}$$

Assuming $\bar{C}_P$ and $\bar{C}_v$ to be temperature-independent, we get

$$\Delta S = \int_1^2 dS = n\bar{C}_P \int_1^2 \frac{dT}{T} = n\bar{C}_P \ln \frac{T_2}{T_1} \text{ (CONSTANT PRESSURE)}$$

$$\Delta S = \int_1^2 dS = n\bar{C}_v \int_1^2 \frac{dT}{T} = n\bar{C}_V \ln \frac{T_2}{T_1} \text{ (CONSTANT VOLUME)}$$

These equations enable us to calculate entropy changes due to temperature variation at constant pressure and at constant volume.

Consider the case of a hot body (temperature, T_h) brought in contact with a cold body (temperature, T_c). We know from experience that heat will flow spontaneously from hot to cold body until the temperature is uniform (say T_f). Let us see how the second law can be applied to this problem.

Since the rest of the surroundings do not participate in the heat transfer process, we need to evaluate only the entropy changes of the hot and the cold bodies in order to compute the entropy change of the universe. Also, it is obvious that the process takes place at constant pressure. Thus, the equations given above for a constant pressure process can be utilised. If we assume, for simplicity, that the hot and the cold bodies both contain one mol of the same substance then $T_f = (T_h + T_c)/2$. The entropy changes of the hot and cold bodies are given by

$$(\Delta S)_{\text{hot body}} = \bar{C}_P \ln \frac{T_f}{T_h} \quad \text{and} \quad \Delta(S)_{\text{cold body}} = \bar{C}_P \ln \frac{T_f}{T_c}$$

where $\bar{C}_P$ is the molar heat capacity of the two bodies. The entropy change of the universe is,

$$(\Delta S)_{\text{universe}} = (\Delta S)_{\text{hot}} + (\Delta S)_{\text{cold}} = \bar{C}_P \left(\ln \frac{T_f}{T_h} + \ln \frac{T_f}{T_c} \right) = \bar{C}_P \ln \frac{T^2_f}{T_h T_c}$$

The term $T^2_f/T_h T_c$ can be analysed in the following manner. We know that, $T_h > T_c$, therefore $T_h - T_c > 0$ and $(T_h - T_c)^2 > 0$ or, $(T^2_h + T^2_c - 2T_h T_c) > 0$.

Therefore, $(T^2_h + T^2_c + 2T_h T_c) > 4T_h T_c$ or, $(T_h + T_c)^2 > 4T_h T_c$ and $\left(\frac{T_h + T_c}{2} \right)^2 > T_h T_c$.

Since $(T_h + T_c)/2 = T_f$, $T^2_f > T_h T_c$ or $T^2_f/T_h T_c > 1$.

This means that $\bar{C}_P \ln \dfrac{T^2_f}{T_h T_c}$, and therefore $(\Delta S)_{universe}$ is greater than zero. This shows that the heat flow from the hot to the cold body is a spontaneous process. Further when $T_h = T_c$, $T^2_f / T_h T_c = 1$. In this situation, $(\Delta S)_{universe}$ will be zero showing thereby that when temperature becomes uniform, equilibrium is attained.

9.11 ENTROPY AND DISORDER

The definition of entropy and the statement of the second law is all that is necessary to analyse the direction and the equilibrium in natural processes. The macroscopic approach that we have used so far for the development of the second law does not, however, provide any insight into the entropy concept. To remedy this situation we now turn to the microscopic picture.

In the case of energy, we found that macroscopic energy is just the sum total of energy of the microscopic units. In the case of entropy, however, it would be meaningless to associate entropy with each individual microscopic unit. Entropy is a statistical property, i.e. it is a property, which at the microscopic level, is not connected with individual atoms and molecules, but with collection of atoms and molecules.* We shall now show that entropy is essentially a measure of (microscopic) disorder in a system.

Let us consider some common examples to establish the connection between entropy and disorder. Suppose we take a number of white balls and black balls in two compartments separated by a partition in a container. When the partition is removed and the container shaken, the white and black balls are mixed. The initial ordered arrangement thus gets converted into a disordered arrangement where the white and black balls are randomly distributed. Note that whereas disorder results spontaneously from order, it is not possible to recover the ordered arrangement by merely shaking the container. The only way to get back the initial arrangement is to individually pick out the white and black balls and put them in separate compartments.

As a second example, consider a deck of cards. Arrange the four suits in a definite sequence (e.g. spades, hearts, diamonds and clubs) and then within each suit arrange the thirteen cards in a definite progression (e.g. 2,3,4,. . . J, Q, K, A). Fifty-two cards placed like this constitute an ordered sequence and we can give the precise location of any particular card in the deck. Now shuffle the deck. The cards get mixed and a disordered sequence is obtained where it is not possible to assign a definite location to any particular card. Thus a disordered deck results spontaneously, but no amount of shuffling will give back the ordered deck.

These and several other examples show that order gives way to disorder spontaneously. To the extent that entropy also increases spontaneously, it is reasonable to assume that entropy is a measure of disorder. This assumption has been found to be entirely valid and it forms the starting point of the branch of science known as *statistical thermodynamics* which uses statistical molecular approach to derive all thermodynamic equations.

*In this sense entropy is similar to temperature. Since the latter is equal to average kinetic energy of atoms and molecules, it can be only associated with collections (where averages become meaningful) rather than with individuals. Pressure is another example of a statistical property.

A question that naturally arises is 'Why is disorder favoured?' This is easily answered by the following example. If we flip a coin, there is an equal chance that heads or tails will show up. If we flip two coins together (or the same coin twice), there is a chance that two heads or two tails will come but there is twice as much chance of occurrence of one heads and one tails. Why should this happen? The reason is that there is only one way to get two heads or two tails but there are two ways to obtain a heads and a tails (e.g. heads in the first toss and tails in the second and vice versa). For one hundred tosses, occurrence of hundred heads or tails is an extremely improbable (but not impossible) event whereas occurrence of around fifty heads and fifty tails is the most likely (but not absolutely certain) event. This is because there is only one way to get hundred heads but there are $(100 \times 99 \ldots \times 51)/(50 \times 49 \ldots \times 1)$ ways of getting fifty heads. Now all heads and all tails form a completely ordered arrangement while a mixture of heads and tails is a disordered arrangement. Hence we conclude that disorder is more frequent than order because there is only one way to get total order but many ways to get disorder. Since the number of particles in a macroscopic system are of the order of 10^{23}, it is not surprising that the system spontaneously becomes disordered, or in other words its entropy increases.

The connection between entropy and disorder provides ready explanation for entropy changes in different situations. For instance, the increase in entropy with volume is understandable because the larger volume permits more disorder. Similarly, increase in temperature increases the range of speeds that a molecule can have (see Chapter 6) and hence there is greater disorder at higher temperature.* We expect the entropy to increase as solids melt to liquids and liquids vapourise to gases because a liquid is more disordered than a solid and a gas is even more disordered than a liquid. Examples of entropy calculation for phase transformations are given in the next section.

9.12 ENTROPY CALCULATIONS

One can calculate the magnitude of entropy change associated with phase changes quite easily. When ice melts it absorbs 1440 calories of heat per mol at 273 K, and hence entropy increases. When liquid water boils at 373K it absorbs 9648 calories of heat per mol, and therefore entropy increases. Entropy values are commonly given in units of calories per degree. One calorie per mol per degree is sometimes called one entropy unit (eu). Examples of entropy changes accompanying phase transitions as well as temperature changes are given below.

Example 9.7 Calculate the entropy change associated with the vapourisation of 1 mol of C_2H_5OH. The heat of vapourisation of C_2H_5OH is 9.22 kcal/mol and its boiling point is 78.5°C.

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{vap}} = \frac{9.220}{78.5 + 273.15} = \frac{9220}{351.65} = 26.22 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

Example 9.8 Calculate the entropy change associated with the freezing of 0.5 mol of liquid nitrogen. The heat of fusion of solid nitrogen is 172.3 cal/mol at its melting point 63.14 K.

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*Sometimes the terms 'position disorder' and 'motional disorder' are used to indicate the disorder due to volume effect and temperature effect respectively.

$$\Delta S_{\text{freezing}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{melting}}} = \frac{-172 \cdot 3}{63 \cdot 14} = -2 \cdot 73 \text{ cal}^{-1} \text{ deg mol}^{-1}$$

$-\Delta H$ of fusion is used because the heat is given up by the liquid when it freezes. Since 0·5 mol is involved, the entropy change will be half of 2·73 cal deg^{-1} mol^{-1}.

$$\Delta S = 1/2(-2 \cdot 73) = -1 \cdot 365 \text{ cal deg}^{-1}$$

Example 9.9 Solid phosphine, PH_3, undergoes a phase change from β-form to α-form at $-223 \cdot 72°C$ with an absorption of 185·7 calories of heat per mol of the substance. Calculate the entropy change when two moles of β-phosphine are converted to α-phosphine.

$$\Delta S_{\beta \to \alpha} = \frac{2 \times 185 \cdot 7}{-223 \cdot 72 + 273 \cdot 15} = \frac{2 \times 185 \cdot 7}{49 \cdot 43} = 7 \cdot 514 \text{ cal deg}^{-1}$$

Example 9.10 Molar heat capacity of CD_2O (deuterated form of formaldehyde CH_2O) is 14 calories at 1000 K. Calculate the entropy change associated with the cooling of 3·2 g of CD_2O vapour from 1000 to 900 K at constant pressure.

$$\text{Molecular mass of } CD_2O = 12 + (2 \times 2) + 16 = 32$$

3·2 g of CD_2O vapour, therefore, contains $(3 \cdot 2/32) = 0 \cdot 1$ mol

$$\text{Hence } \Delta S = (0 \cdot 1)\, \overline{C}_p \ln \frac{T_2}{T_1} = 0 \cdot 1 \times 14 \times 2 \cdot 303 \log \frac{900}{1000} = -1 \cdot 479 \text{ cal deg}^{-1}$$

Example 9.11 Diamond (carbon) has a heat capacity of 1·45 cal deg^{-1}mol^{-1} at 25°C. Calculate the entropy change when *Koh-i-noor* weighing 100 carats (21 g) undergoes a temperature change from 25° to 26°C irreversibly.

Atomic mass of carbon is 12, and 2 g of diamond is therefore equivalent to $21/12 = 1 \cdot 75$ mol.

$$\Delta S = 1 \cdot 75\, \overline{C}_p \ln \frac{T_2}{T_1} = 1 \cdot 75 \times 1 \cdot 45 \times 2 \cdot 303 \log \frac{299}{298} \simeq 0 \cdot 1 \text{ cal deg}^{-1}$$

9.12.1 Trouton's Rule

Although heats of vapourisation of liquids vary over a considerable range, an interesting generalisation was pointed out by Trouton (1884) which is known as *Trouton's rule*. According to this rule, the heat of vapourisation (ΔH_{vap}) in calories per mol divided by the boiling point of the liquid on the absolute scale (T_b), i.e. the entropy of vapourisation is a constant equal to 21 cal deg^{-1} mol^{-1}.

$$\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T_b = 21 \text{ cal deg}^{-1}\text{mol}^{-1} = 21 \text{ eu} = \text{TROUTON CONSTANT}$$

This equation is useful for estimating the molar heat of vapourisation of a liquid of known boiling point.

Values of ΔH_{vap} and ΔS_{vap} listed in Table 9.2 show that while this rule is often applicable, it is not always obeyed. It might be expected that different liquids may have about the same entropy of vapourisation at the boiling point, provided there is no association or dissociation upon vapourisation. Substances that deviate greatly from the rule include (*i*) low-boiling liquids such as hydrogen and helium which boil only a little above 0 K, (*ii*) polar substances such as water and alcohol which form hydrogen-bonded liquids and exhibit high boiling points as well as high ΔH_{vap}, particularly the latter (such liquids have entropies of vapourisation higher than 21 eu) and (*iii*) liquids such as acetic acid whose molecules are partially associated in the vapour

Table 9.2 Entropies of Vapourisation

Substance	Normal boiling point, °C	Heat of vapourisation, ΔH_{vap} kcal mol^{-1}	Entropy of vapourisation, ΔS_{vap} cal deg^{-1}mol^{-1}(eu)
He	−268·94	0·020	4·7
H$_2$	−252·97	0·216	10·6
H$_2$O	100	9·717	26·04
HF	19·9	1·8	6·1
C$_2$H$_5$OH	78·5	9·22	26·22
CH$_3$COOH	118·3	5·82	14·3
n-Butane (C$_4$H$_{10}$)	−0·5	5·32	19·63
n-Hexane (C$_6$H$_{14}$)	68·74	6·896	20·17
n-Octane (C$_8$H$_{18}$)	125·66	8·36	20·96
Benzene (C$_6$H$_6$)	80·1	7·353	20·81
Toluene (C$_7$H$_8$)	110·6	8·0	20·85
Cyclohexane (C$_6$H$_{12}$)	80·7	7·19	20·3

phase (these have entropies of vapourisation less than 21 eu). In the case of non-polar liquids Trouton's rule is applicable. For such liquids, it provides a means of estimating vapour pressures over a range of temperatures from a knowledge of their normal boiling points.

Thus far, all the calculations of entropy changes we have made involved only single substances and variation of temperature.

Example 9.12 A hydrocarbon boils at 350 K at 1 atm pressure. Estimate its heat of vapourisation.

According to Trouton's rule, $\Delta H_v/T_b = 21$ cal mole,$^{-1}$ i.e.

$$\Delta H_v = T_b \times 21 = 350 \times 21 = 7350 \text{ cal mol}^{-1}$$

9.12.2 Absolute Entropies and the Third Law of Thermodynamics

One of the characteristic features of thermodynamics is that it deals with only changes in the value of functions like energy and enthalpy. As already shown, it is enough to specify these changes with respect to some (arbitrarily chosen) standard state; the absolute value of energy or enthalpy cannot be assigned from thermodynamic arguments. However, the entropy function is an interesting exception to this rule. Thanks to the third law of thermodynamics, the absolute entropies, which are of importance in many applications, can be assigned. The third law is usually stated in the form: *The entropy of a perfect crystal of every element or compound is zero at 0 K.*

The third law statement is easy to understand from the molecular viewpoint. As temperature is lowered, disorder should decrease. At the lowest permissible temperature of 0 K, it is reasonable that disorder, and hence entropy vanishes and a perfectly ordered state is obtained.

We have discussed earlier in this section the calculation of entropy changes during phase transitions and due to temperature and pressure variation. Combining this with the knowledge that entropy of a pure substance is zero at 0 K, it is possible to calculate absolute entropy of any substance at 1 atm and 298 K. These are referred to as *absolute entropies* $(S°)$ in the standard state. Values of absolute entropies for some substances are given in Table 9.3. It can be seen that the entropies of gases are higher than that of liquids and that of liquids

Table 9.3 Values of Absolute Entropies (in cal deg^{-1} mol^{-1}) of Substances in the Standard State at 298 K

GASES							
	H$_2$	32·21	HCl	44·64	CH$_4$	44·50
	He	30·13	HBr	47·44	C$_2$H$_6$	54·85
	N$_2$	45·77	CO	47·20	C$_2$H$_4$	52·45
	O$_2$	49·01	CO$_2$	51·08	C$_2$H$_2$	48·00
	F$_2$	48·49	NO	50·34	C$_6$H$_6$	64·34
	Cl$_2$	53·29	NH$_3$	46·01	C$_6$H$_{12}$	71·28
LIQUIDS	Hg	18·17	Br$_2$	36·4	H$_2$O	16·73
SOLIDS	C(*graphite*)	1·37	Al	6·77	I$_2$	27·76
	C(*diamond*)	0·6	Ca	9·95	Si	4·51
			Fe	6·49	NaCl	17·3

are higher than that of solids. Diamond, which is one of the hardest substances known, has one of the lowest entropy values which is consistent with its highly ordered structure.

9.13 FREE ENERGY

We have shown in section 9.10 that the entropy function can be used as a criterion of spontaneity for processes taking place in an isolated system. Since the entire universe is an isolated system (by definition), the entropy criterion can be used for processes provided entropy changes of both the system and the surroundings are taken into account. There are many situations where this procedure becomes cumbersome and it is, therefore, very useful to reformulate the spontaneity criterion in such a manner that only the system need be considered. Several functions known as free energy functions have been invented for this purpose; each function serves as a spontaneity criterion under some specified condition. We shall consider only one such free energy function, called the *Gibbs free energy function* (denoted by the symbol G) which is useful for processes taking place at constant temperature and constant pressure. Since the latter restrictions apply to most chemical phenomena, Gibbs function is widely used in chemical thermodynamics.

The Gibbs function is defined as

$$G = H - TS = E + PV - TS$$

It is obvious that G should be an extensive state function.

$$dG = dE + PdV + VdP - TdS - SdT$$

At constant T and P, $(dG)_{T,P} = dE + PdV - TdS$

But $dE + PdV = dq$ (first law) and $TdS = dq_{rev}$ (second law)

$\therefore (dG)_{T,P} = dq - dq_{rev}$

For a reversible process, $dq = dq_{rev}$, while for an irreversible process $dq < dq_{rev}$. Hence it follows that,

$$dG = 0 \text{ (REVERSIBLE PROCESS)} \quad \text{and} \quad dG < 0 \text{ (IRREVERSIBLE PROCESS)}$$

Since irreversibility is linked to spontaneity, and reversibility is connected with equilibrium, one can say that if free energy change of a system for a process is less than zero (i.e. negative), the process is spontaneous; if the free energy change is zero, the system is in equilibrium. In other words, at constant temperature and pressure, the free energy of a system decreases in a spontaneous process, but remains constant when equilibrium is reached. We have thus arrived at the spontaneity criterion without considering the surroundings explicitly.

9.13.1 Significance of Free Energy

We have so far considered systems which are capable of doing only the pressure-volume (i.e. mechanical) work. However, there are chemical systems which deliver non-mechanical work also. For example, an electrochemical cell yields electrical work. The free energy function has a simple interpretation under such circumstances. Consider the equation,

$$(dG)_{T,P} = dE + PdV - TdS$$

If a system does both mechanical and non-mechanical (say electrical) work, the first law has the form

$$\delta q = dE + \delta w = dE + \delta w_m + \delta w_{elec}$$

where the total work δw is written as the sum of mechanical work, δw_m, and o electrical work, δw_{elec}. Under reversible condition, at constant temperature and pressure, we have

$$dq_{rev} = dE + PdV + dw_{elec}$$
$$\text{or } dE = dq_{rev} - PdV - dw_{elec}$$

Substituting this value of dE in the equation for dG, and noting that $dq_{rev} = TdS$, we get

$$(dG)_{T,P} = dq_{rev} - PdV - dw_{elec} + PdV - Tds = -dw_{elec}$$
or
$$-(dG)_{T,P} = dw_{elec}$$

which means that the decrease in free energy of a system is equal (at constant T and P) to the reversible non-mechanical work done by the system.

The equation for finite change in G is

$$\Delta G = \Delta H - T\Delta S \text{ (constant } T)$$

It is clear that one of the situations where ΔG is negative is when ΔH is negative (enthalpy decreases) and ΔS is positive (entropy increases), i.e. the lowering of energy and the increase in disorder favour spontaneity. It should be noted, however, that consideration of enthalpy and of entropy *separately* cannot decide the spontaneity or the equilibrium in natural processes. The energy of a system can increase (positive ΔH) in a spontaneous process provided the disorder also increases to an extent to make ΔG negative. Similarly, the system can become more ordered (ΔS negative) provided ΔH decreases even more. At equilibrium, the two terms exactly compensate each other and that is why we have $\Delta G = 0 = \Delta H - T\Delta S$ at equilibrium. We thus see that the equilibrium state is a state of compromise where the two tendencies in nature, namely, tendency to go towards a state of lowest potential energy and tendency to increase entropy (disorder), exactly balance each other.

Let us consider the example of vapourisation of water: (i) At its normal boiling point, $T_b (=373K)$, water is in equilibrium with its vapour. Under these conditions, $\Delta G = 0$ and therefore $\Delta H = T\Delta S$. The entropy of

vapourisation at the boiling point is, $\Delta S_{\text{vap}}=\Delta H_{\text{vap}}/T_b$. (*ii*) For temperatures higher than the boiling point, $\Delta H_{\text{vap}}<T\Delta S_{\text{vap}}$ since $T>T_b$. (Here we have assumed that both ΔH and ΔS are constant.)   It follows that ΔG will be negative, i.e. vapourisation will be spontaneous above the boiling temperature. (*iii*) Similarly, ΔG will be positive if T is lower than the boiling point; the vapourisation will accordingly be not spontaneous.   However, ΔG for the reverse process of condensation will now be negative; condensation will, therefore, be spontaneous below the boiling temperature.

9.13.2 Standard Free Energies

Like standard heats of formation or heats of reaction we can define standard free energies of formation of subtsances and standard free energy changes of reactions. For defining standard states, the convention followed is the same as the one used with enthalpies, i.e. the standard state is the most stable state of the substance at 298 K and 1 atm pressure. The standard free energy change of a reaction is the free energy change involved when the reactants and the products are in their standard states. Similarly, the standard free energy of formation of a compound refers to the free energy change involved in the formation of the compound from its elements when all the participating substances are in their standard states. Thus, the standard free energy of formation of gaseous NO_2, ΔG°_f, corresponds to the reaction,

$$\tfrac{1}{2}(N_2(g)+O_2(g)\rightarrow NO_2(g)\quad \Delta H^\circ_f=12\cdot39 \text{ kcal.}$$
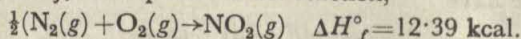
Like standard heats of formation, standard free energies of formation of elements are taken as zero. Free energies of formation of some substances at 298 K are given in Table 9.4. Since at constant temperature, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, we can readily calculate standard free energy changes by employing data on standard entropy and enthalpy changes. Using ΔG°_f data, we can calculate the free energy change of chemical reactions. For example, for the reaction between acetylene and hydrogen to form ethane,
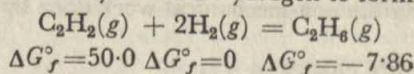
$$C_2H_2(g) + 2H_2(g) = C_2H_6(g)$$
$$\Delta G^\circ_f=50\cdot0 \quad \Delta G^\circ_f=0 \quad \Delta G^\circ_f=-7\cdot86$$
$$\Delta G^\circ\text{reaction}=\Delta G^\circ_f(C_2H_6 g)-\Delta G^\circ_f(C_2H_2 g)=-7\cdot86-50\cdot0=-57\cdot86 \text{ kcal}$$

Since a negative free energy change (or free energy decrease) is directly linked with spontaneity, we can say from the above example that when the reaction involves substances in standard states, the hydrogenation reaction of acetylene to form ethane will proceed spontaneously. This qualification of standard states is essential because for other conditions ΔG value will be different, and unless it is known what the specific conditions of the system are, it is not possible to determine ΔG and predict the direction in which a given reaction will proceed.

9.13.3 Dependence of Free Energy on Pressure and Temperature

For a reversible process the general expression for free energy change is

$$dG=dE+PdV+VdP-TdS-SdT$$

The first two terms are equal to q_{rev} and $q_{rev}=TdS$. Therefore,

$$dG = VdP - SdT$$

At constant pressure $(dP = 0)$, $dG = -SdT$

or,

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

Since the entropy of a substance is always a positive quantity, the left-hand side of the equation which represents the temperature coefficient of free energy, is always negative. This means that for all substances, an increase in temperature causes a decrease in free energy.

At constant temperature, $dT=0$ and $dG=VdP$, or $\left(\frac{\partial G}{\partial P}\right)_T = V$.

Table 9.4 Standard Free Energies of Formation of Some Compounds ($\Delta G°_{298}$ kcal/mol)

NO(g)	20·72	CO(g)	−32·81	$C_2H_6(g)$	−7·86
$NO_2(g)$	12·39	$CO_2(g)$	−94·26	$C_2H_2(g)$	50·06
$N_2O(g)$	−24·76	$CH_4(g)$	−12.14	$C_6H_6(g)$	30.97
$H_2O(g)$	−54·63	$C_2H_4(g)$	16·28	$C_6H_6(l)$	29·76
$H_2O(l)$	−56·69				

Since the volume of a substance is always a positive quantity, we should expect an increase in free energy with increase in pressure.

For an ideal gas, it is simple to calculate the extent of free energy change as a function of pressure.

$$dG_T = VdP$$

If the pressure changes from P_1 to P_2,

$$\int_1^2 dG_T = \Delta G_T = G_2 - G_1 = \int_{P_1}^{P_2} VdP = nRT \int_{P_1}^{P_2} dP/P$$

$$= nRT \ln (P_2/P_1)$$

If the system involves one mol of the substance, and the initial pressure is 1 atm then G_1 refers to the standard state and can be replaced by $G°$. The final pressure can be taken as any pressure P and the corresponding free energy G. Then, $\bar{G}_T - \bar{G°}_T = RT \ln (P/1)$, or, $\bar{G}_T = \bar{G°}_T + RT \ln P$. This gives a direct relationship between free energy and pressure at a given temperature.

Example 9.13 (a) For a chemical reaction, the values of ΔH and ΔS at 300 K are −10 kcal and 20 cal deg^{-1} respectively. What is the value of ΔG of the reaction? (b) Assuming that ΔH and ΔS remain constant calculate the ΔG value at 400 K.

(a) $\Delta G = \Delta H - T\Delta S$
$= -10,000 - 300 \times 20 = -10,000 - 6,000 = -16,000$ cal

(b) When $T = 400$ K,
$\Delta G = -10,000 - 400 \times 20 = -10,000 - 8,000 = -18,000$ cal

Example 9.14 A liquid freezes into a solid ($\Delta H = -1000$ cal mol^{-1}) at 200 K and 1 atm. (a) What is the value of ΔG at 200 K? (b) What is the ΔS value at 200 K? (c) Will the freezing be spontaneous at 150 K and 1 atm? (d) What is the sign of ΔG at 250 K and 1 atm?

(a) $\Delta G = 0$ at 200 K since the system is at equilibrium
(b) $\Delta S = \Delta H/T = -1000/200 = -5$ cal deg^{-1}
(c) Assuming that ΔH and ΔS are constant,
$$\Delta G = \Delta H - T\Delta S$$
$$= -1000 - 150 (-5) = -1000 + 750 = -250 \text{ cal mol}^{-1}$$

Since ΔG is negative, freezing will be spontaneous at 150 K. This is what we would expect since 150 K is below the freezing point (200 K).

(d)   When T is 250 K,
$$\Delta G = -1000 - 250\ (-5) = 250\ \text{cal mol}^{-1}$$
ΔG is positive and freezing will not be spontaneous.

9.13.4 Free Energy Change and Equilibrium Constant

Let us consider the following general reaction consisting of four ideal gases A, B, C and D:

$$aA(g, p_A) + bB(g, p_B) = cC(g, p_C) + dD(g, p_D)$$
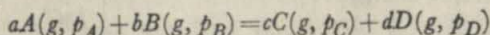
The free energy change in the reaction can be obtained by substracting the total free energy of the reactants from that of the products. Thus,

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

Since $G_{\text{products}} = c \times \bar{G}_C + d \times \bar{G}_D$ and $G_{\text{reactants}} = a \times \bar{G}_A + b \times \bar{G}_B$, we have
$\Delta G = c\bar{G}_C + d\bar{G}_D - a\bar{G}_A - b\bar{G}_B$.

At constant temperature, the free energy at a given pressure P is related to the standard state free energy by the relation, $\bar{G} = \bar{G}° + RT \ln P$. In this case, if we apply this relation to all the reactants and products, the above equation for the free energy change (ΔG) in the reaction becomes,

$$= c(\bar{G}°_C + RT \ln p_C) + d(\bar{G}°_D + RT \ln p_D) - a(\bar{G}°_A + RT \ln p_A) - b(\bar{G}°_B + RT \ln p_B)$$

$$= (c\bar{G}°_C + d\bar{G}°_D - a\bar{G}°_A - b\bar{G}°_B) + cRT \ln p_C + dRT \ln p_D - aRT \ln p_A - bRT \ln p_B$$

$$= \Delta G° + RT\ (\ln p^c_C + \ln p^d_D - \ln p^a_A - \ln p^b_B)$$

$$= \Delta G° + RT \ln \frac{p^c_C\, p^d_D}{p^a_A\, p^b_B}$$

We see that the change in free energy, ΔG, depends on the standard free energy change $\Delta G°$ and the partial pressures of products and reactants.

Under equilibrium conditions $\Delta G = 0$ and the free energy equation becomes,

$$0 = \Delta G° + RT \ln \left[\frac{p^c_C\, p^d_D}{p^a_A\, p^b_B} \right]_{\text{equilibrium}}$$

Now $\Delta G°$ is a characteristic property of the reaction system and it has a constant value at a given temperature. It follows that the expression within the brackets in the above equation will also be a characteristic constant of the system. Since it refers to the equilibrium condition it is called the *equilibrium constant*. The equilibrium constant is represented by the symbol K. Rearranging the above equation we can write,

$$\Delta G° = -RT \ln K$$

where
$$K = \left[\frac{p^c_C\, p^d_D}{p^a_A\, p^b_B} \right]_{\text{equilibrium}}$$

It should be noted that the relation given above between $\Delta G°$ and equilibrium constant can be derived for reactions in solutions also. In the latter cases, K is usually expressed in some appropriate concentration units. (The symbols K_p, K_c or K_x are often used to indicate that the equilibrium constant expression contains partial pressures, molar concentrations or mole fractions respectively.) It should also be noted that the relation $\Delta G° = -RT \ln K$ is not restricted to chemical reactions; it is equally applicable to physical transformations like a phase change. It is obvious that when $\Delta G°$ is negative, K is a greater than unity which means that the products are in excess at equilibrium. Similarly, a positive $\Delta G°$ means that K is less than unity. i.e. the reactants are in excess at equilibrium.

Example 9.15 (*a*) In an equilibrium reaction when will ΔG° be equal to zero? (*b*) When will ΔG° be negative for an equilibrium reaction? (*c*) When will ΔG° be positive? (*d*) Estimate K at 300 K when ΔG° is -1200 cal mol^{-1}.

(*a*) $\Delta G^\circ = -RT \ln K$

If $K=1$, $\ln K=0$ and $\Delta G^\circ=0$, i.e. G° will be zero when K is unity.

(*b*) $\Delta G^\circ = -RT \ln K$

Since RT is positive, ΔG° will be negative only when $\ln K$ is positive; $\ln K$ will be a positive quantity only when K is greater than unity.

(*c*) Following the arguments similar to (*b*), ΔG° will be positive when K is less than unity.

(*d*) $\Delta G^\circ_{300} = -R \times 300 \ln K$

$\ln K = -\Delta G^\circ_{300}/R \times 300$

$\log K = \dfrac{1200}{600 \times 2\cdot303} = 0\cdot868$ or $K=7\cdot4$

9.13.5 Position of Equilibrium

We have already pointed out that there are two thermodynamic quantities which are of importance in discussing equilibria, the internal energy and the entropy. If the equilibrium in a reaction is to lie predominantly on the right-hand side (i.e. the product side), a highly negative ΔG° is desirable. We can use this criterion to derive some information on the nature of energy and entropy changes that must take place. Consider the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = \text{NEGATIVE NUMBER (for equilibrium to lie}$$
$$\text{on the product side)}$$

For ΔG° to be negative, according to the above relation, $T\Delta S^\circ$ should be positive, while ΔH° should be negative.

What is meant by a positive $T\Delta S^\circ$? Since T is always positive, for $T\Delta S^\circ$ to be positive, ΔS° has to be positive; this means that the entropy of the products must be significantly larger than that of the reactants. Or, in general, a high entropy of the products will lead to more product yield in a given reaction.

Similarly, a negative ΔH°, which can be approximately taken for ΔE°, means that products must have less energy than the reactants for the reaction to continue in the forward direction. So a loss in energy in a reaction is helpful for shifting the equilibrium to the right.

Thus, in the overall picture, *a reaction is driven to the product side either by an increase in entropy or by a decrease in energy.* When both these quantities are favourable (i.e. ΔH° is negative and ΔS° is positive), the equilibrium constant is very high and the reaction virtually goes to completion. In other cases, when one of the quantities is favourable, the equilibrium constant has a moderate value.

Very often, however, the magnitude of ΔH° is several times more than $T\Delta S^\circ$. In such situations, the sign and magnitude of ΔG° is almost entirely determined by the sign and magnitude of ΔH°. If ΔH° is highly negative (i.e. the reaction is exothermic), we have a large equilibrium constant. Likewise, for endothermic reactions, ΔH° is positive, and this shifts the equilibrium to the left. For liquid and solid systems, where $\Delta S^\circ \cong 0$, this is predominantly the case. Although it is convenient to be able to predict the equilibrium position knowing only the value of ΔH° of the reaction, one has to be careful in this regard to ascertain whether $T\Delta S^\circ$ contribution is small, and hence negligible.

SUGGESTED READING

B. H. Mahan, *Elementary Chemical Thermodynamics*, Benjamin, New York, 1963.

L. K. Nash, *Elements of Chemical Thermodynamics*, Addison-Wesley, Reading, Mass., 1962.

G. C. Pimentel, *Understanding Chemical Thermodynamics*, Holden-Day, Inc., California, 1969.

J. Waser, *Basic Chemical Thermodynamics*, Benjamin, New York, 1966.

PROBLEMS

9.1   Which of the following quantities are state functions?

(i) q, (ii) w_{rev}, (iii) $q-w$, (iv) $E+H$, (v) q_{rev}/T, (vi) q/w, (vii) E, (viii) $H+PV$.

9.2   Calculate the amount of work done, heat absorbed, and change in internal energy in a reversible isothermal expansion of 0·5 mol of nitrogen gas from 5 to 1 atm at 27°C. Assume ideal behaviour.

9.3   One gm atm of Zn is placed in excess of dil. H_2SO_4 at 27°C in a cylinder fitted with a piston. Find the values of E, q, and w for the process if the area of the piston is 500 cm² and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given out to the surroundings is 36·5 kcal.

9.4   Cyclopropane, $C_3H_6(g)$, has a heat combustion equal to 499·85 kcal mol⁻¹ at 25°C and 1 atm. Using the heats of formation $\Delta H°_f H_2O(g)$ and $\Delta H°_f CO_2(g)$ from Table 9.1 calculate the heat of formation of cyclopropane.

9.5   The value of ΔH for the following reaction is $-31·9$ cal. Assuming ϵ_{C-C} as 82·6 kcal mol⁻¹, calculate ϵ_{C-H}.

$$
\begin{array}{c}
CH_3 \\
| \\
CH_3-C-CH_3 + (11/2)O_2 \rightarrow 5CO_2 + H_2O \\
| \\
CH_3
\end{array}
$$
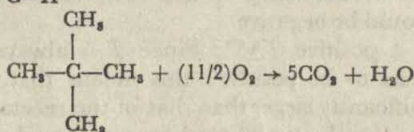
9.6   Calculate the value of ΔH of the following reaction from bond energy data:

$$
\begin{array}{c}
H_3C \qquad\qquad CH_3 \\
| \qquad\qquad\qquad | \\
CH-CH=CH-CH + HCl \\
| \qquad\qquad\qquad | \\
H_3C \qquad\qquad CH_3
\end{array}
\rightarrow
\begin{array}{c}
H_3C \qquad\qquad\qquad CH_3 \\
| \qquad\qquad\qquad\qquad\quad | \\
CH-CH-CH-CH \\
| \quad | \quad | \quad\quad | \\
H_3C \; H \; Cl \; CH_3
\end{array}
$$
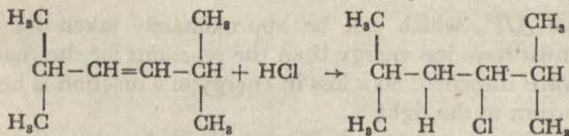
9.7   The electron affinity (A) of a substance such as Cl may be defined as the change in enthalpy for the reaction

$$Cl^- = Cl + e \qquad \Delta H = A$$
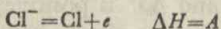
Calculate the electron affinity of chlorine, using the Born-Haber thermochemical cycle for sodium chloride given the following data:

Crystal energy (or lattice energy) of NaCl, $\Delta H_{cryst} = 185$ kcal/mol
Standard heat of formation of NaCl, $\Delta H°_f = -99$ kcal/mol
Heat of sublimation of Na, $\Delta H°_{sub} = 26$ kcal/mol
Dissociation energy of Cl_2, $D_{Cl-Cl} = 58$ kcal/mol
Ionisation energy of Na, $IE_{Na} = 117$ kcal/mol

9.8   The 'proton affinity' P of a substance such as NH_3 may be defined as the change in enthalpy for the reaction

$$NH^+_4(g) = NH_3(g) + H^+(g) \qquad \Delta H = P$$
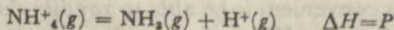
P_{NH_3} may be computed from other thermal data through consideration of the Born-Haber cycle given below. (All substances except NH_4Cl are in gaseous state.)

$$NH_4Cl(s) \xrightarrow[\hspace{3cm} (1) \hspace{3cm}]{E} NH_4^+(g)+Cl^-(g)$$

(5)

$\Delta H°_f$

(2) $\Bigg\downarrow P_{NH_3}$

$NH_3(g)+H^+(g)+Cl^-(g)$

(3) $\Bigg\downarrow -I_H+ECl$

(4)

$\frac{1}{2}N_2(g)+2H_2(g)+\frac{1}{2}Cl_2(g) \longleftarrow \hspace{2cm} NH_3(g)+H(g)+Cl(g)$
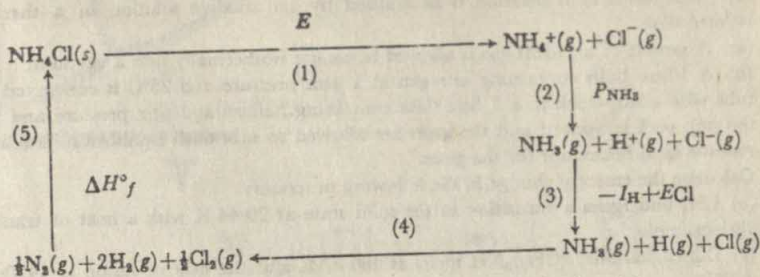
Lattice energy of crystalline NH_4Cl,	$E = 153$ kcal mol^{-1}
Ionization energy of hydrogen atom	$I_H = 312$ kcal mol^{-1}
Electron affinity of chlorine atom,	$A_{Cl} = 9\cdot25$ kcal mol^{-1}
Heat of formation of $NH_4Cl(s)$	$\Delta H°_f = -75\cdot1$ kcal mol^{-1}
Heat of formation of $NH_3(g)$	$\Delta H°_f = -10\cdot9$ kcal mol^{-1}
Dissociation energy of Cl_2,	$D_{Cl-Cl} = 58$ kcal mol^{-1}
Dissociation energy of H_2,	$D_{H-H} = 104$ kcal mol^{-1}

Calculate the value of P_{NH_3}. Write the thermal data you need to compute the enthalpy change in the step during path 4.

9.9 (a) Using the bond energy data given below, estimate the heat of formation of gaseous isoprene

$$\underset{\underset{CH_3}{|}}{H_2C=C-\overset{\overset{H}{|}}{C}=CH_2}$$
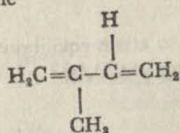
$\epsilon_{C-H}=98\cdot8$ kcal mol^{-1} $\epsilon_{C-C}=83\cdot1$ kcal mol^{-1} $\epsilon_{C=C}=147\cdot0$ kcal mol^{-1}

Heat of sublimation of carbon (graphite) $=171\cdot7$ kcal mol^{-1}

$\epsilon_{H-H} =104$ kcal mol^{-1}

(b) Using the combustion data given below, calculate heat of formation of gaseous isoprene.

   (i) Heat of combustion of gaseous isoprene
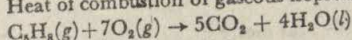
$$C_5H_8(g)+7O_2(g) \rightarrow 5CO_2 + 4H_2O(l)$$
$$\Delta H=-745\cdot8 \text{ kcal mol}^{-1}$$

   (ii) Heat of formation of $CO_2(g)$ $\Delta H=-94\cdot1$ kcal mol^{-1}
   (iii) Heat of formation of $H_2O(l)$ $\Delta H=-68\cdot3$ kcal mol^{-1}

(c) Explain why the values of heats of formation of gaseous isoprene obtained in (a) and (b) are different.

9.10 Calculate the wavelength of radiation which is just sufficient to break each of the following bonds:

H—H bond $\epsilon_{H-H} = 104$ kcal mol^{-1}

O—H bond $\epsilon_{O-H} = 111$ kcal mol^{-1}

I—I bond $\epsilon_{I-I} = 36$ kcal mol^{-1}

In what regions of the spectrum (infrared, visible, or ultraviolet) would these wavelengths be found?

9.11 1 kg stone at 27°C falls 100 m into a lake whose temperature is 27°C. Find the entropy change of (a) the stone, (b) the lake and (c) the universe. Repeat the above problem for the case when the stone is lowered reversibly into the lake and compare the loss in available energy in the two cases.

9.12 For each of the following processes, state which of the quantities, ΔE, ΔH, ΔS, or ΔG are equal to zero. Give reason for your conclusions.

   (i) Liquid water is vapourised at 100°C and 1 atm pressure.

(*ii*) An aqueous acid solution is neutralised by an alkaline solution in a thermally isolated flask.

(*iii*) A sample of an ideal gas is allowed to escape isothermally into a vacuum.

(*iv*) A 1 litre bulb containing nitrogen at 1 atm pressure and 25°C is connected by a tube with a stop-cock to a 2 litre flask containing helium at 1 atm pressure and 25°C, the stop cock is opened and the gases are allowed to mix until equilibrium is reached. Assume ideal behaviour for the gases.

9.13 Calculate the entropy change in the following processes:

(*a*) CH_4 undergoes a transition in the solid state at 20·44 K with a heat of transition 18·1 cal/mol.

(*b*) Dimethylamine, $(CH_3)_2NH$ melts at 180·97 K and the heat of fusion is 1420·1 cal mol^{-1}.

9.14 (*a*) For a chemical reaction, ΔH and ΔS at 25°C are −45 kcal and −50·5 cal/deg respectively. What is the value of ΔG at this temperature?

(*b*) If it is assumed that ΔH and ΔS do not change significantly for a 75° rise in temperature, what is the value of ΔG at 100°C?

9.15 Calculate the free energies at 25°C for the following, using the table of free energies of formation: (*a*) Ethane at 10^2 atm pressure; (*b*) water at 10^{-4} atm pressure and (*c*) carbon dioxide at 110^{-8} atm pressure.

9.16 At 10 atm pressure and 450°C the value of K for the equilibrium system $N_2+3H_2 \rightleftharpoons 2NH_3$ is 0·0066. What is the value of $\Delta G°$ of this reaction at this temperature and pressure?

9.17 Calculate the value of $\Delta G°$ of the following reaction using $\Delta G°_f$ values from the standard data:

$$CO(g) + 1/2 O_2(g) \rightleftharpoons CO_2(g)$$
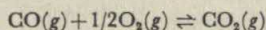
9.18 In Problem 9.17, which direction will the reaction go to attain equilibrium if a system contains 1 atm of $CO(g)$, 0·5 atm of $O_2(g)$ and 0·01 atm of $CO_2(g)$?

9.19 Given the reaction

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow HCl(g)$$
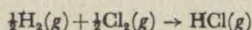
Assuming ideal behaviour for all the gases and using the data given below (*i*) calculate ΔH value for the reaction at 298 K, (*ii*) calculate the value of C_p of H_2, Cl_2 and HCl (assume that all the degrees of freedom contribute to the specific heat), (*iii*) calculate ΔH value for the reaction at 398 K, and (*iv*) calculate K value for the reaction at 298 K.

DATA:

Bond energy of $H_2(g)$	= 104 kcal mol^{-1}
Bond energy of $Cl_2(g)$	= 58 kcal mol^{-1}
Bond energy of $HCl(g)$	= 102 kcal mol^{-1}
Entropy of $H_2(g)$ at 298 K	= 31·21 cal deg^{-1}
Entropy of $Cl_2(g)$ at 298 K	= 53·3 cal deg^{-1}
Entropy of $HCl(g)$ at 298 K	= 44·6 cal deg^{-1}

P ⊥ T
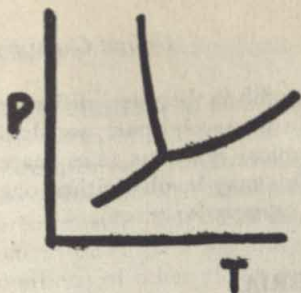
10

Equilibrium-I: Phase and Chemical Equilibria

In the huge manufactory of natural processes, the principle of entropy occupies the position of manager, for it dictates the manner and method of the whole business, whilst the principle of energy merely does the book-keeping, balancing credits and debits.

ROBERT EMDEN

Lavinia: *Then what can we do*
      When we can go neither back nor forward? Edward!
      What can we do?
Reilly: *You have answered your own question,*
      Though you do not know the meaning of what you have said.
Edward: *Lavinia, we must make the best of a bad job.*
      That is what he means.

The Cocktail Party, T. S. ELIOT

At equilibrium, the free energy of a process, whether it be a physical change like a simple phase transition or a chemical reaction, does not undergo any change (see Chapter 9). For example, in a phase change (say liquid to vapour) the molar free energies in the two phases are equal at equilibrium; in other words, the free energy change is zero. An equally important aspect of equilibrium systems is *reversibility*. While dealing with liquids (Chapter 8), we pointed out that the vapour pressure of a liquid results from the evaporation and condensation processes occurring reversibly. At equilibrium, the two processes take place with equal rates and the two phases remain indefinitely. Like phase changes, many chemical reactions are also reversible. Under certain conditions of temperature and concentration, products coexist with reactants at equilibrium . In reversible reactions, we reach the same equilibrium state regardless of the direction from which it is approached.

Based on the above principles, we shall now discuss the nature of equilibrium systems. We shall treat the subject matter in two parts. The first

341

part on *phase equilibria* will deal with physical equilibria between different states of matter of one or more chemical species. In the second part, we shall consider those equilibrium systems in which chemical reactions take place between various species present in the system. This may involve either one phase (*homogeneous system*) or more than one phase (*heterogeneous system*).

10.1 BASIC CONCEPTS OF PHASE EQUILIBRIA

Before we discuss the nature of phase equilibria in detail, it is necessary to understand the definitions of some of the basic terms as well as the principles governing equilibria.

10.1.1 Phase

Any homogeneous part of a system is called a *phase*. This means that throughout a phase, all physical and chemical properties are uniform. A system may consist of one phase or more than one phase. A system containing only liquid water is an example of one-phase system. If the system contains some water vapour in addition, it will be a two-phase system. If besides liquid and water vapour, the system also contains some solid ice, the number of phases will be three. The ice present in the system may be present as a single block or in many pieces, but the number of phases, P, always remains three. In other words, any physical discontinuity of a phase does not change the number of phases present in a system. In a mixture of oil and water, the system is full of innumerable small oil drops dispersed in water, but it is a two-phase system. By *number of phases* we simply mean the number of *different* types of phases present in the system.

The above concept of phase is applicable to systems containing any number of chemical species. A solution of sodium chloride and water contains only one phase. But a saturated solution of sodium chloride in water in contact with excess solid sodium chloride will be considered as having two phases. A mixture of powdered tin and lead has two phases ($P=2$), but if the mixture is melted and solidified, the resulting solid having uniform composition and properties throughout, will be a one-phase ($P=1$) system. Similarly, a mixture of solid sodium chloride, potassium nitrate and barium sulphate constitutes three phases ($P = 3$). Solid sulphur occurs in the monoclinic and rhombic forms, each having well defined physical properties different from the other. A mixture of monoclinic and rhombic sulphur is considered to have two phases ($P = 2$).

If two different liquids are mixed, the number of phases will depend on their miscibility. If water and ethyl alcohol are mixed, the number of phases will be one since they are completely miscible. However, if water and carbon tetrachloride are mixed, the number of phases are two, because these liquids are not very miscible at ordinary temperatures. The resulting mixture separates into two layers ($P = 2$), one containing a small amount of carbon tetrachloride dissolved in a large amount of water and the other containing a small amount of water in a large excess of carbon tetrachloride.

Since all gases mix freely, the resulting number of phases is always one ($P = 1$), no matter how many gases are mixed.

10.1.2 Number of Components

The chemical composition of a given phase may be expressed in terms of the concentration of individual species present in it. If the concentrations of all the species present in all the phases are known, it is obvious that the system is completely defined as far as the chemical composition is concerned. Quite often, the equilibrium composition of some phases can be predicted if the compositions of other phases in the system are known. Then the system can be completely defined with a fewer number of concentration variables than is necessary in a case where concentrations of all species in all phases are independently known. In other words, there are a certain number of *independent concentration variables* in a system with the help of which the chemical composition of the entire system can be defined. The rest of the concentration variables are dependent, and it is redundant to have separate information on them since any variation of the independent concentration variables automatically predetermines the course of the variation of dependent variables. One is, therefore, interested in the *minimum number of concentration variables needed to define the system completely*. This number is defined as the *number of components* and is represented by C. We should be careful in the use of the term components, because it is *not necessarily* identical with the number of distinct *chemical species* present in the system as exemplified below.

Let us consider a system of liquid water in equilibrium with water vapour at a given temperature and pressure. Since there is only one concentration variable, that involving water, it is a one-component system, or $C = 1$. In a system consisting of a solution of sodium chloride in water, we cannot have a complete idea of the system unless we know how much of sodium chloride and how much of water are used to make the solution. A knowledge of both the quantities is essential. This involves two independent concentration variables and is, therefore, a two-component system, or $C = 2$. If we had a saturated solution of sodium chloride in contact with solid sodium chloride and water vapour, it would be a three-phase system, but still comprising two components because the need for information on both sodium chloride and water still remains. Similarly a solution containing potassium nitrate, sodium nitrate and water is an example of a three-component system.

Let us now examine examples where the number of components C is less than the number of distinct chemical species present in the system. Suppose we take ammonia in a container and raise the temperature of the system sufficiently high so that ammonia decomposes as follows:

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$
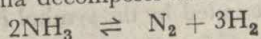
The equilibrium constant for this reaction, in terms of partial pressures of the constituents, is given by (see section 9.13.4)

$$K = \frac{p_{N_2} \, p^3_{H_2}}{p^2_{NH_3}}$$

Since the equilibrium constant is a characteristic constant of the system at a given temperature, the numerator and the denominator on the right-hand side of the above equation bear a definite relationship with each another. Of the three pressure terms that appear on the right-hand side, if two are known, the third one is automatically fixed. This is a two-component system although the number of chemical species present in the system is three. There is, however, an additional peculiarity in the specific example we are considering. Since we

started with pure ammonia which decomposed partially into nitrogen and hydrogen, for every molecule of nitrogen formed three molecules of hydrogen are formed simultaneously. We, therefore, have the relationship between the partial pressures of nitrogen and hydrogen $3p_{N_2} = p_{H_2}$. On this basis, we can write

$$K = \frac{p_{N_2}\, p^3_{H_2}}{p^2_{NH_3}} = \frac{p_{N_2}\, (3p_{N_2})^3}{p^2_{NH_3}} = \frac{27p^4_{N_2}}{p^2_{NH_3}}$$

Now, information on one of the right-hand side variables fixes the value of the other. This means that, *if the initial condition is specified*, there is only one independent concentration variable, hence $C = 1$, whereas in the general case where initial conditions are not known, $C = 2$. Whenever chemical reactions take place between the constituents of a system and some equilibrium relationships can be worked out between them, the number of components can be known without difficulty. We must realise, however, that it is the *number* of components that is important, not their chemical nature. For example, in the case cited above, when $C = 1$, it may refer to any one of the species NH_3, H_2 or N_2. Before such equilibrium relationships are used to determine the number of components, we must ensure that equilibrium conditions are indeed present in the system.

10.1.3 Degrees of Freedom

We have defined the minimum number of independent concentration variables needed to describe the composition of each phase as the number of components. Even if we know the number of components, the system is not completely defined in all respects. For example, information on the composition of various phases does not convey information about important properties like the temperature and pressure of the system. Temperature and pressure are intensive variables since they do not depend on the amount of substance under consideration. Besides temperature and pressure, there are many other intensive properties like density, or refractive index that characterise a system. Concentration, which we have already considered, is also an intensive variable. It is not necessary, however, to have information on all the intensive variables. For complete definition of a given system, a knowledge of a certain minimum number of intensive variables is required. This minimum number of intensive variables with the help of which the system can be completely defined are called the *degrees of freedom*, represented by the symbol F.

To illustrate this, we shall first choose a one-phase, one-component system consisting of a pure gas, i.e. involving only one kind of chemical species. The system can be completely defined with the help of any *two* of the three quantities, temperature, pressure and density or concentration. We have seen earlier that these quantities are related to each other by an equation of state, and if we know the values of any two of them, temperature and pressure, or pressure and density, etc., the third quantity can be found out easily. Alternatively we can say that only two of the intensive variables can be varied independently, or the degree of freedom $F = 2$.

Let us take a system consisting of pure liquid carbon tetrachloride in equilibrium with its own vapour. Since the vapour pressure is dependent on the temperature, and a knowledge of one leads to another, the degree of freedom

$F = 1$. This means that only one of these two intensive variables (vapour pressure and temperature) can be independently varied.

10.1.4 Phase Rule

The relation between the number of phases P the number of components C, and the number of degrees of freedom F, was first derived by J. Willard Gibbs. This relationship, known as the *Phase Rule*, is stated as follows:

$$F = C - P + 2$$

10.2 PHASE DIAGRAM OF ONE-COMPONENT SYSTEMS

We have seen in Chapter 9 that the free energy change is related to a change in pressure and temperature through the following equation:

$$dG = VdP - SdT$$

For a single component system containing one mole of a substance this equation can be written as

$$\overline{dG} = \overline{V}dP - \overline{S}dT$$

where the bar represents molar quantities (e.g. $\overline{V}$ = molar volume). Here $\overline{dG}$ defines the change in the free energy and thus the equilibrium situation of a system. From the above equation, we notice that a variation in free energy can be brought about by a change in temperature or pressure, or both. If we consider a one-component system, these two variables T and P, become the only degrees of freedom that can be varied independently. In such a one-component system, according to the phase rule, the number of phases that can be realised is a maximum of three. If the system is in any one phase, both temperature and pressure can be varied. At constant temperature, a plot of the molar free energy change against P for each phase would give a different line and similarly a plot of the free energy change against T would give yet another line for each phase. We may combine the variation of the free energy change with P and T for each phase in a three-diamensional diagram, where each phase would yield a particular surface characterised by its $\overline{V}$ and $\overline{S}$. The way in which these surfaces meet in any equilibrium situation may be expressed by the phase diagram of water shown in Fig. 10.1.

Fig. 10.1 Pressure-temperature diagram of water (not drawn to scale)

24
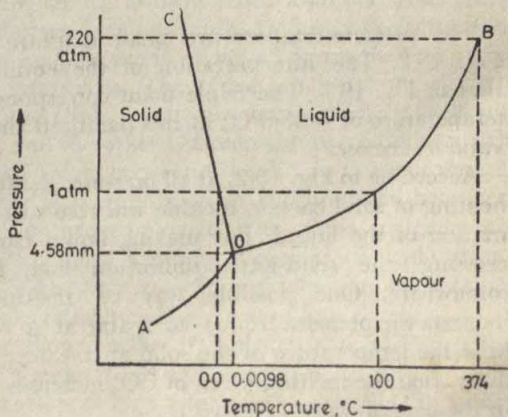
In Fig. 10.1, the line CO represents the points of equal molar free energy between ice and liquid water, AO between ice and vapour and BO between liquid water and vapour. These equilibrium lines represent lines of equal free energy. We see that the line CO has a negative slope; this is because the molar volume of the liquid is smaller (density higher) than that of the solid. (This is a situation peculiar to water.) Interestingly, these three lines meet at a point O. The point O is unique since fixed values of P (4·58 mm) and T (0·0098°C) are associated with it. At this point, since both the degrees of freedom, P and T, are fixed, the water system has no degrees of freedom left — meaning thereby that at O the system is in simultaneous equilibrium with all the three phases. This point O is thus *invariant* and is a characteristic phase rule constant of water. This point is referred to as the *triple point*. Triple points are characteristic thermodynamic invariance points of a system and because of this property, they can be used in the formulation of temperature scales.

Fig. 10.1 also shows the normal melting point (0°C) and boiling point (100°C) of water at 1 atm pressure. From the figure it is seen that the boiling point increases with increase in pressure; the melting point of ice however, decreases with increase in pressure (since the molar volume of the liquid is smaller than ice).
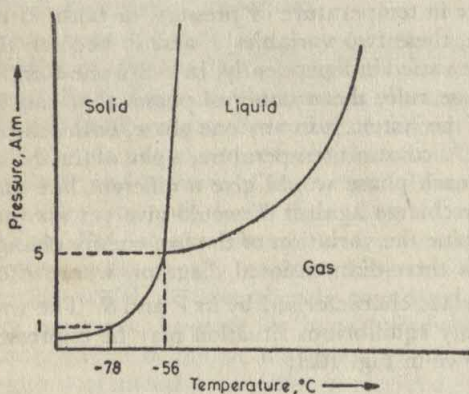
Fig. 10.2 Pressure-temperature diagram of CO_2 (not drawn to scale)

The pressure-temperature phase diagram of carbon dioxide is shown in Fig. 10.2. The interpretation of the equilibria in this case is similar to that in Fig. 10.1. The triple point corresponds to a pressure of 5 atm and a temperature of −56·6°C; at this point, all the three phases (solid, liquid and vapour) coexist.

According to Fig. 10.2, at all pressures less than 5 atm (triple point pressure), heating of solid carbon dioxide will result in sublimation and not in the formation of the liquid. For making liquid carbon dioxide, we have to avoid crossing the solid-gas equilibrium line, but cross the liquid-solid line somewhere. One possible way of making liquid carbon dioxide is to increase the pressure from 1 to 6 atm at a temperature of −90°C and then raise the temperature of the solid at constant pressure until it melts. Fig. 10.2 shows that the melting point of CO_2 increases with increase in pressure, unlike in the case of water (Fig. 10.1).

It is instructive to examine how the phase rule is helpful in defining the properties of a system. Each of the lines in Figs. 10.1 and 10.2 represents two phases in equilibrium ($P = 2$) since we are dealing with a one-component system, $C = 1$. According to the phase rule, $F = C - P + 2 = 1 - 2 + 2 = 1$. This means that only one intensive variable can be changed independently, and when this is done, the other variables are automatically fixed. At the triple point, there are three phases and $P = 3$. Hence, $F = C - P + 2 = 1 - 3 + 2 = 0$. That is, no variables can be changed if equilibrium between three phases is to be maintained.

It is also possible that many solid (or liquid) phases may coexist under special equilibrium situations, depending on temperature and pressure conditions. As pointed out earlier (Chapter 7), a chemical substance can exist in more than one physical form. Since these physical forms have different physical properties, each one of them constitutes a distinct phase. Although water under moderate temperatures and pressures has only three phases—solid, liquid and vapour— at high pressures, a number of solid phases (different ice structures) are formed. These new solid phases are named ice II, III, etc., ordinary ice being taken as ice I. This is illustrated in Fig. 10.3. The point b is the triple point between the liquid, vapour and ice I. Points c, e, f, g, h, i are the other triple points.

Fig. 10.3 Pressure-temperature diagram of water in the high pressure range showing the existence of various forms of ice
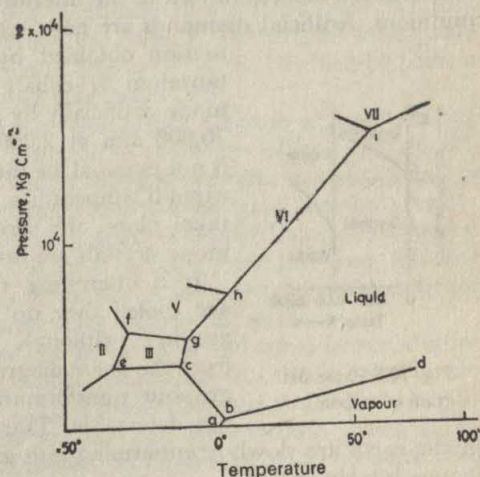
Although many substances are known to have more than one solid phase, one usually finds only one liquid phase for a substance. Helium is one interesting substance which exists in two different kinds of liquid forms, helium I and helium II with characteristic properties. The phase diagram of helium is shown in Fig. 10.4. There are two triple points, one between the solid, liquid helium I and liquid helium II, and the other between the two liquids and the vapour. We see that there is no contact between the solid and vapour regions. One consequence of this is that it is impossible to sublime solid helium no matter what physical conditions are employed. The phase diagram also indicates that liquid helium II is the most stable form even at 0 K and ordinary pressures. Only by applying high pressures can solid helium be obtained. One of the fascinating properties of helium II is its very low viscosity.

The phase diagram of carbon shown in Fig. 10.5 clearly shows that graphite is the stable form at ordinary temperatures and pressures. In order to form diamond from graphite, application of high pressures is essential. In nature,
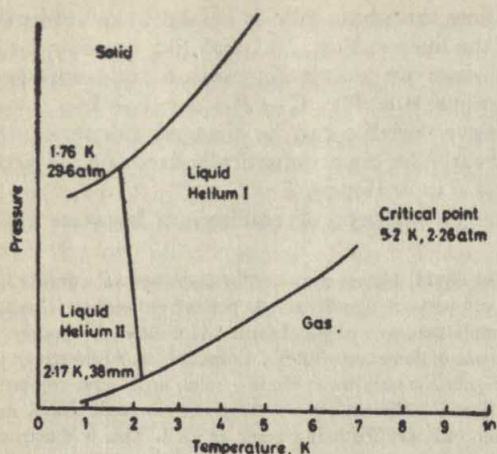
Fig. 10.4 Phase diagram of helium

diamonds are indeed formed in the interior of the earth under high pressure conditions. Artificial diamonds are now made commercially using this information obtained by phase rule. In the presence of tantalum or cobalt catalysts, diamonds have been made artificially by application of a pressure of about 70,000 atm at 2,000°C. Although high temperature is not essential for the transformation, the conversion is rapid if temperature is raised. After the transformation takes place, the system is cooled and synthetic diamond crystals are isolated.
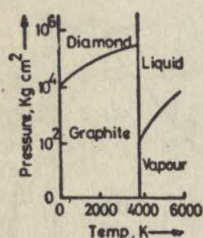
Fig. 10.5 Phase diagram of carbon

It is interesting that when hot diamond crystals are cooled they do not immediately revert back to graphite, although this is what one would expect from the phase diagram. This is because the diamond-graphite transformation is so slow a process that it is not detectable. Thus, while all the diamond crystals on the earth are slowly transforming into graphite, it appears to us as if no change is taking place.

10.3 PHASE DIAGRAMS OF SYSTEMS WITH MORE THAN ONE COMPONENT

Phase diagrams of systems with more than one component provide valuable information about the conditions of equilibria between the various components and their phases. With several components present, a multitude of phases can exist, each with distinctive properties. For the synthesis of materials with special properties, phase diagrams provide important information. A typical phase diagram of a two-component system is shown in Fig. 10.6.

In a system comprising two components, there exists an additional degree of freedom. This is the composition of the system, usually expressed as a weight fraction or mole fraction. The advantage in using this unit is that once the mole fraction of one component (B) is known, that of the other (A) is automatically fixed, since the sum of the mole fractions is unity. The phase diagram

Fig. 10.6 Typical phase diagram of a two-component system. This type of phase diagram is exhibited by many metal pairs like bismuth+cadmium or lead+tin. The temperatures corresponding to points A and B are the melting points of A and B. Curve BE gives the temperatures and concentrations at which pure solid B is in equilibrium with a A-B solution. Curve AE represents the temperatures and concentrations at which pure A is in equilibrium with the solution. Point E is called the *eutectic point*. Any point on the curve AE or BE represents the temperature at which A or B begins to crystallise out (at the specific composition given by the x-axis). Below temperatures represented by $S_1 S_2$, mixtures of pure solids A and B of appropriate composition would be present.

Mole fraction of B
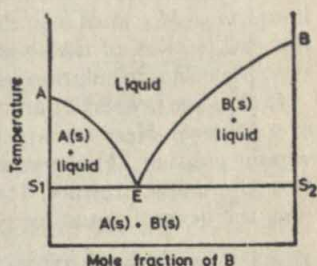
of a two-component system would in theory be three dimensional since pressure, temperature and composition are the three independent intensive variables. Usually for convenience, we fix the pressure constant (1 atm) and plot the phase diagram as a two-dimensional plot as in Fig. 10.6. While lines AE and BE are the equilibrium lines between the homogeneous liquid phase and solid A, and liquid and solid B respectively, the point E, termed the *eutectic point*, is an invariant point with no degrees of freedom. At E, the melting point of the mixture is lower than that of either pure component.

The iron-carbon phase diagram is an example of a system of great technical importance. Addition of carbon changes the properties of iron considerably and various grades of steel with widely varying physical properties can be made depending on the carbon content. With the addition of a third component like chromium, further variations of physical properties can be achieved. The manufacture of stainless steel is an important example along this line. In the extraction and purification of metals multi-component phase diagrams provide important information on methods that can be used.

As long as two substances interact under some conditions to form a solution or a compound, one can construct phase diagrams. In other words, for any combination of substances, there exists a phase diagram which describes the equilibria between the components involved and their various phases. In the next section we shall consider some interesting properties of solutions involving two components.

10.4 COLLIGATIVE PROPERTIES OF SOLUTIONS

There are some interesting properties of dilute solutions which have important applications. A peculiarity of these properties is that they do not depend on the nature of the solute, but only on the number of molecules in the solution. Thus, two different solutions which have different kinds of substances as solutes but identical mole fractions, behave similarly in some ways. This dependence of the property of a solution solely on the mole fraction of the solute can be expressed as:

PROPERTY MEASURED ∝ MOLE FRACTION OF THE SOLUTE

If we represent the mass of the solute by w_A, mass of solvent by w_B, and their respective molecular masses by M_A and M_B, we can write,

$$\text{PROPERTY MEASURED} = (\text{CONSTANT}) \times \frac{w_B/M_B}{w_B/M_B + w_A/M_A}$$

A measurement of the appropriate property of a solution will thus enable the determination of the molecular mass M_B of the solute, since we generally know w_A, M_A and w_B. Properties of this type which depend only on the mol fraction of the solute, i.e. on the relative proportion of solute and solvent molecules in solution, are called *colligative properties*.

Colligative properties are widely used for determination of molecular masses of substances. Here we will outline four colligative properties: (*a*) lowering of vapour pressure, (*b*) elevation of boiling point, (*c*) depression of freezing point, and (*d*) osmotic pressure. It will be of interest to note in the following sections, how the general equation given above is used in widely different situations.

10.4.1 Lowering of Vapour Pressure and Raoult's Law

If we take a pure liquid and place it in a closed container, we find that a part of the liquid evaporates and fills the available space with the vapour. The vapour exerts a pressure on the walls of the container and equilibrium between the liquid and the vapour is established. This pressure is the *vapour pressure* of the liquid. This characteristic property of the substance increases with tempera ture. If the liquid is heated to sufficiently high temperature so that its vapou-pressure equals the external pressure exerted on it, the liquid boils. Accordingly, with a high external pressure we expect a high boiling point and with a reduced external pressure, a low boiling point (see Chapter 8 for a detailed discussion).

If a solute is added to a liquid to make a binary solution consisting of two components, the vapour pressure of the solvent undergoes a change. Since the vapourisation process occurring on the solution surface would depend on the composition of the solution, we may expect that the partial pressure of the vapour of each component of the solution will depend on its molefraction in solution. Thus, if the solvent and solute have molefractions x and x_B respectively in solution, their parial pressures in the vapour above the solution would be,

$$p_A \propto x_A \qquad p_B \propto x_B$$

where p_A and p_B are vapour pressures of the solvent and solute respectively. We see that vapour pressures actually correspond to concentration terms. This is why there is a lowering in the vapour pressure of the solvent whenever a solute is added to a solvent.

Based on experimental vapour pressure data, Raoult in 1886 showed that the above relationships are given by

$$p_A = p°_A x_A \quad \text{and} \quad p_B = p°_B x_B$$

where $p°_A$ and $p°_B$ represent the vapour pressures of the pure liquids. This is usually referred to as *Raoult's law*. The total vapour pressure over the solution is given by $p_A + p_B$. When these relationships are obeyed, we have *ideal solutions*. According to the equations given above, a plot of partial vapour pressure versus mol fraction will give straight lines for both the components. This is shown in Fig. 10.7(*a*) for the benzene-toluene system which represents an ideal solution of two volatile liquids.

Very often, solutions do not demonstrate ideal behaviour. Ideal behaviour can be expected at best in those cases where the two components are chemically indifferent towards each other, i.e. they have neither great affinity nor strong repulsive forces between them. When intermolecular attractive forces are pre-
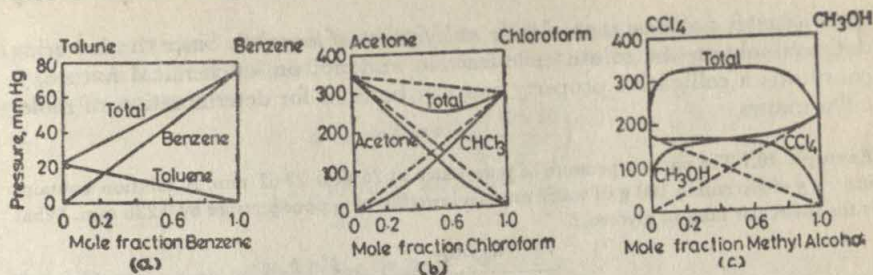
Fig. 10.7 Vapour pressure-composition diagrams of binary liquid mixtures: (a) benzene–toluene mixture; the system behaves ideally; (b) acetone–chloroform mixture; this system shows a negative deviation from Raoult's law; and (c) methanol–carbon tetrachloride mixture; this system exhibits positive deviation from ideality. Broken lines represent ideal behaviour.

dominant, there will be association of molecular species. An example of such intermolecular attraction is the hydrogen bonding that exists between acetone and chloroform in the liquid phase. The total vapour pressure of the solution will, therefore, be less than what it would have been in the ideal case and we will get a negative deviation from Raoult's law. This is shown in Fig. 10.7(b). Examples of solutions where this type of non-ideality is seen include nitric-acid–water, hydrochloric acid–water, and acetone–chloroform systems. When intermolecular forces are negligible, but intramolecular forces are predominant, we observe just the opposite effect, and the vapour pressure of the solution will be more than what it would have been in the ideal case. In such a case we observe positive deviation from Raoult's law (Fig. 10.7c). An example of positive deviation is the system methanol–carbon tetrachloride.

Many of the non-ideal binary solutions exhibit maxima or minima in their vapour pressure-composition curves. A maximum in the vapour pressure-composition curve corresponds to a minimum in the boiling point-composition curve and vice versa. The compositions corresponding to maximum or minimum boiling points are referred to as constant boiling mixtures or *azeotropes*. At this composition, the vapour and liquid will have the same compositions. A typical example of an azeotrope is 20·22 per cent (by weight) solution of hydrocholoric acid in water.

When a non-volatile solute is present in a solution, the situation is somewhat different. In such a case, Raoult's law can be applied only to the solvent, and the solvent vapour pressure p_A should be nearly equal to the total vapour pressure. Since there is no contribution from the solute, the vapour pressure of the solution decreases with the decreasing mole fraction of the solvent. This can be written as

$$p = p_A = p^\circ_A x_A$$

where p°_A is the vapour pressure of the pure solvent and x_A is the mole fraction of the solvent. The above equation can also be written as

$$p^\circ_A = p^\circ_A (1 - x_B) \text{ or } (p^\circ_A - p_A)/p^\circ = x_B$$

Here, x_B is the mole fraction of the solute and $x_A = 1 - x_B$. We note that $(p^\circ_A - p_A)$ represents the absolute lowering of vapour pressure and $(p^\circ_A - p_A)/p^\circ_A$ represents the relative lowering with respect to the vapour pressure of the pure solvent. With this relationship involving the non-volatile solute, Raoult's law can be stated as follows. *The relative lowering of vapour pressure*

of the solvent in a solution is equal to the mole fraction of the solute. Since the lowering depends only on the solute mole fraction and not on its chemical nature, it constitutes a colligative property and can be used for determination of molecular masses.

Example 10.1 The vapour pressure of pure water at 25°C is 23·62 mm. A solution containing 9·2 g of glycerol in 180 g of water causes a lowering of vapour pressure by 0·236 mm. What is the molecular mass of glycerol?

$$\frac{w_G/M_G}{w_G/M_G + w_W/M_W} = \frac{p° - p}{p°}$$

Since it is a dilute solution, we can neglect w_G/M_G in comparison with w_W/M_W which is equal to $180/18 = 10$. The molecular mass of glycerol is,

$$M_G = w_G \frac{M_W}{w_W} \frac{p°}{p° - p}$$

$$= (9·2) \cdot \frac{(18)}{(180)} \frac{(23·62)}{0·236} = 92$$

10.4.2 Elevation of Boiling Point

Lowering of the vapour pressure of a liquid by addition of a solute has some interesting consequences. One of them is the elevation of the boiling point. The normal boiling point of a liquid is the temperature at which the vapour pressure is equal to 1 atm. Since the vapour pressure is lowered due to the addition of the solute, we need to heat the solution to a higher temperature for the vapour pressure to reach 1 atm than what would have been necessary in the case of the pure solvent. This is the reason why we observe an elevation of the boiling point in a solution compared to that of the pure solvent. If ΔT_b represents the rise in boiling point, then we have the relation,

$$\Delta T_b = K x_B$$

where K is a constant. When the molality of the solute (moles of solute in 1 kg of solvent) rather than the mole fraction is used, this expression becomes,

$$\Delta T_b = K_b m$$

Here m represents the molality of the solute and K_b is referred to as the *molal boiling point elevation constant*. The values of K_b for a few common solvents are given in Table 10.1.

Table 10.1 Molal Boiling Point Elevation Constants of Solvents

Solvent	BP °C	K_b (degree/molal)	Solvent	BP °C	K_b (degree/molal)
Water	100	0·51	Acetone	56·1	1·71
Methyl alcohol	64·7	0·86	Ether	34·6	2·02
Ethyl alcohol	78·4	1·22	Acetic acid	118·3	3·07
Benzene	80·1	2·53	Chloroform	61·3	3·63

Example 10.2 10 g of a paraffin wax dissolved in 100 g of benzene raises the boiling point by 1°. What is the molecular mass of the wax?

Let the molecular mass of the wax be M. Then, the number of moles of wax present in 100 g of benzene is $10/M$. In 1000g of benzene, therefore, $10 \times (10/M)$ moles of wax will be present. Hence we can write

$$\Delta Tb = K_b m = K_b \left(\frac{10 \times 10}{M} \right)$$

$$\text{or} \qquad M = \frac{100 K_b}{\Delta T_b} = \frac{100 \times 2 \cdot 53}{1} = 253$$

10.4.3 Depression of Freezing Point

Another consequence of the lowering of vapour pressure is the depression of freezing point. A solution has a lower freezing point than the pure solvent and the lowering, ΔT_f, is proportional to the mole fraction of the solute:

$$-\Delta T_f = K x_B$$

When molality of the solute is used,

$$-\Delta T_f = K_f m$$

where K_f is the *molal freezing point depression constant*. Molal freezing point depression constants of some solvents are given in Table 10.2. Thus, for one molal solution of naphthalene in benzene we can expect a freezing point depression of $5 \cdot 12°$. Due to experimental difficulties with the measurement of boiling point elevation, freezing point depression is more commonly used for the determination of molecular masses.

Table 10.2 Molal Freezing Point Depression Constants of Solvents

Solvent	FP °C	K_f degree/molal	Solvent	FP °C	K_f (degree/malal)
Water	0·00	1·86	Acetic acid	16·6	3·57
Benzene	5·5	5·12	Dioxane	11·7	4·71
Cyclohexane	6·5	20	Naphthalene	80·1	6·98
Camphor	173	40			

Example 10.3 What would be the depression of freezing point if 7·8 g of a hydrocarbon with molecular formula $C_{12}H_{12}$ is dissolved in 100 g of liquid naphthalene?

$$-\Delta T_f = K_f m$$

Molality of the hydrocarbon is equal to $(7 \cdot 8/156) \times (1000 / 100) = \frac{1}{2}$. Hence, the lowering of freezing point $-\Delta T_f = 6 \cdot 98 \times \frac{1}{2} = 3 \cdot 49°$ C

10.4.4 Osmotic Pressure

The fourth colligative property pertains to the process that takes place when a solution and solvent are separated by a semipermeable membrane. Such a membrane permits the movement of solvent molecules, but not of solute molecules. In such a situation, the solvent molecules flow from the solvent side to the solution
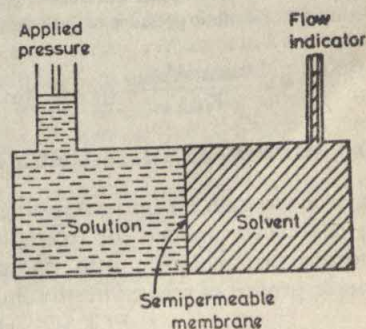
Fig. 10.8 Schematic diagram of an osmometer

side through the membrane (Fig. 10.8). This process is known as *osmosis*. The movement of solvent molecules in osmosis stops when the hydrostatic pressure on the solution side is sufficiently high to prevent the flow of the solvent. This extra pressure on the solution side necessary to counteract the forces of osmosis is called *osmotic pressure*. The osmotic pressure, π, of a solution, being a colligative property, is proportional to the mole fraction of the solute.

$$\pi = \frac{RT}{\bar{V}_A} x_B$$

where $\bar{V}_A$ is the molar volume of the solvent A. If R is expressed in litre atm, T in Kelvin and $\bar{V}_A$ in litres, the osmotic pressure will be in atmospheres. Since $x_B = n_B/(n_A + n_B)$, the mole fraction x_B can be approximated by n_B/n_A in the case of dilute solutions. The osmotic pressure relationship then becomes,

$$\pi = RT\ \frac{n_B}{n_A\bar{V}_A} = RT\ \frac{n_B}{V} = cRT$$

where c represents the molar concentration of the solute and $n_A\bar{V}_A = V$, the volume of the solution itself, since the solution is dilute.

Many processes which occur in living organisms, both animal and vegetable, depend on osmosis through membranes of cell walls that surround them. One of the chief uses of osmotic pressure measurements is the molecular mass determination of high molecular mass compounds like polymers and biologically important molecules.

Example 10.4 A 10 g sample of a polymer dissolved in 1 litre of water shows an osmotic pressure of 2×10^{-3} atm at 300 K. Estimate the molecular mass of the polymer from these data.

$$\pi = cRT = \frac{w_{polymer}/M_{polymer}}{n_{water}\ \bar{V}_A}\ RT = \frac{w_{polymer}/M_{polymer}}{V_{solution}}\ RT$$

$$M_{polymer} = \frac{w_{polymer}\ RT}{\pi\ V_{solution}} = \frac{10\times0.082\times300}{2\times10^{-3}\times1} = 123,000$$

Example 10.5 How much dextrose ($C_6H_{12}O_6$) must be dissolved in one litre of water to yield a solution of osmotic pressure of 7.65 atm at 37°C?

$$\pi = \frac{w_{solute}/M_{solute}}{V_{solution}}\ RT,\ \text{or}\ w_{solute} = \frac{\pi\ V_{solution}\ M_{solute}}{RT} = \frac{7.65\times1\times180}{0.082\times310} = 54.2\ g$$

10.5 HOMOGENEOUS CHEMICAL EQUILIBRIA

In order to gain an understanding of reactions involving chemical equilibria, we shall first consider the example of the gas phase decomposition of phosphorous pentachloride into phosphorous trichloride and chlorine and the reverse process of recombination into phosphorous pentachloride.

$$PCl_5(g)\ \rightleftharpoons\ PCl_3(g) + Cl_2(g)$$
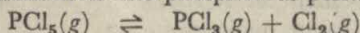
In order to evolve a qualitative understanding of the nature of the equilibrium in this reaction system, let us assume that the system initially consisted of one

mol of PCl_5 in a one-litre container. If the system is left to itself, we can expect the following changes to take place: PCl_5 will begin to decompose, and as a result, equivalent amounts of PCl_3 and Cl_2 will be formed. However, since the reaction of PCl_3 and Cl_2 forms PCl_5, as soon as some PCl_3 and Cl_2 are formed from PCl_5, part of them will react to regenerate some PCl_5. With the passage of time, more PCl_5 will decompose to form more of PCl_3 and Cl_2 and consequently the total amount of PCl_5 regenerated will also increase.

We recognise two opposing trends in this reaction. One concerns the decomposition of PCl_5. At the outset, we start with only PCl_5 and it decomposes to give PCl_3 and Cl_2. As time proceeds, one expects a depletion of PCl_5 and eventually no PCl_5 would be left at all. The rate with which PCl_5 decomposes depends on its concentration and hence the rate will show a decrease from an initial high value to zero after a while. However, during the reaction, PCl_3 and Cl_2 are formed. These two can react by the reverse reaction (again with a rate depending on their concentrations) to replenish the PCl_5. In other words PCl_5 is decomposing at a varying rate, and simulataneously is being replenished at another varying rate, both reactions depending on the concentrations of the species. One may thus visualise a concentration situation where the two reactions occur with equal rates balancing each other. Such a situation is termed a state of *dynamic equilibrium*. In this equilibrium state, both the forward and the backward reactions are taking place, but with equal rates. There is no *net* detectable change in the concentrations of the species in equilibrium. An example of dynamic equilibrium that we have encountered before is that of vapourisation of liquids (Chapter 8).

Now let us take the example in which we start from equimolar proportions of the products PCl_3 and Cl_2 and follow the processes step by step up to the equilibrium condition. We will see that here also complete conversion of PCl_3 and Cl_2 to PCl_5 does not take place. When all reactions appear to have ceased, some PCl_3 and Cl_2, are left unreacted. For a given total mass of the system, the equilibrium composition, i.e. the amount of PCl_5, PCl_3, and Cl_2 present in the equilibrium system, is independent of the direction from which we approach the equilibrium. No matter where a PCl_5-PCl_3-Cl_2 system may be, there is a spontaneous trend towards the equilibrium composition. The exact equilibrium composition, as we will see later, depends on the initial concentration conditions as well as on external conditions like temperature.

With this qualitative understanding about the nature of chemical equilibria, we can now explore some quantitative aspects of equilibrium systems. In Chapter 9 we have seen that spontaneity and free energy change in a reaction are closely related. If ΔG is negative, the reaction will spontaneously proceed in the forward direction. If ΔG is positive, it will spontaneously proceed in the reverse direction. If ΔG is equal to zero, it means that the system has reached an equilibrium state, and no further observable change can take place. Under this equilibrium condition, the ratio of the concentrations of products to reactants is fixed and this is termed the *equilibrium constant*, K_c. For the PCl_5-PCl_3-Cl_2 system, the equilibrium expression can be written in terms of the equilibrium concentrations of PCl_5, PCl_3 and Cl_2:

$$K_c = \frac{[PCl_3]_{eq}\,[Cl_2]_{eq}}{[PCl_5]_{eq}}$$

We can readily recognise that the above equation is the same as what is conventionally described as the *law of mass action*. The square brackets represent

active masses or generally the concentrations of the reacting species. A change in concentration of any of the species will be balanced by the change in the concentration of another so as to keep K constant.

We had shown in Chapter 9 that the standard free energy change, ΔG° is related to K by, $\Delta G^\circ = -RT \ln K$. In the present case,

$$\Delta G^\circ = -RT \ln \frac{[\ PCl_3\ ]_{eq}\ [\ Cl_2\ ]_{eq}}{[\ PCl_5]_{eq}}$$

If the molar enthalpy change, ΔH°, and the molar entropy change, ΔS°, for the reaction are known we can obtain the value of ΔG° ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$). Once ΔG° value is known, it is an easy matter to calculate the equilibrium constant or relative concentrations of species at equilibrium.

A knowledge of initial concentrations is usually sufficient to obtain detailed information on the composition at equilibrium. We shall illustrate this in the case of the phosphorus pentachloride decomposition equilibrium. Let us initially take 1 mole of PCl_5 in a one-litre container (there will be no PCl_3 and Cl_2). At equilibrium, a fraction of this mole of PCl_5 will have decomposed to form PCl_3 and Cl_2. This fraction, denoted by α, is usually termed the *degree of dissociation*. Thus, the equilibrium concentration of PCl_5, i.e. $[PCl_5]_{eq}$ must be given by $1-\alpha$. Since for every mole of PCl_5 decomposed, one mole of PCl_3 and one mole of Cl_2 are formed, for α moles of PCl_5 lost, α moles of PCl_3 and α moles of Cl_2 are formed. So, $[PCl_3]_{eq} = \alpha$ and $[Cl_2]_{eq} = \alpha$. The equilibrium constant can now be written as

$$K = \frac{[PCl_3]_{eq}\ [Cl_2]_{eq}}{[PCl_5]_{eq}} = \frac{\alpha\ \alpha}{1-\alpha} = \frac{\alpha^2}{1-\alpha}$$

This equation affords a means of evaluating the degree of dissociation from a knowledge of the equilibrium constant. Once the value of K is known, all the equilibrium concentrations are known. Conversely, if α value is known (by chemical analysis) we can calculate the values of K and ΔG°.

In this simple calculation, we took the initial concentrations of PCl_3 and Cl_2 to be equal to zero. If these initial concentrations are different and non-zero, we can still determine equilibrium concentrations of individual species by the above procedure. Let the initial concentrations of PCl_5, PCl_3 and Cl_2 be 1·5, 0·05 and 0·5 mol lit^{-1} respectively. At equilibrium

$$K = \frac{[PCl_3]_{eq}\ [Cl_2]_{eq}}{[PCl_5]_{eq}} = \frac{(0·05+\alpha)\ (0·5+\alpha)}{(1·5-\alpha)}$$

Here again, there is only one unknown and we can readily obtain equilibrium concentrations from the value of K.

The process of attainment of equilibrium can be visualised as a process of adjustment of concentrations of chemical species, so that the overall ΔG is zero. In the present case,

$$\Delta G = \Delta G^\circ + RT \ln \frac{[PCl_3]\ [Cl_2]}{[PCl_5]}$$

Since $\Delta G^\circ = -RT \ln K$, we can rewrite the above expression in the form,

$$\Delta G = -RT \ln \frac{[PCl_3]_{eq}\ [Cl_2]_{eq}}{[PCl_5]_{eq}} + RT \ln \frac{[PCl_3]\ [Cl_2]}{[PCl_5]}$$

This shows that ΔG at any given temperature has a constant term, ΔG°, and a part that shows the status of the reaction with respect to equilibrium. At equilibrium, the second term on the left-hand side will become equal to the first term, and $\Delta G = 0$.

Interesting predictions can be made about the equilibrium position in a reaction system from a knowledge of $\Delta G°$: If $\Delta G°$ is positive, K will be small and less than unity and there will be negligible decomposition of PCl_5; if $\Delta G°$ is negative, K will be greater than unity; this implies that there will be appreciable decomposition of PCl_5 to PCl_3 and Cl_2.

We have seen that a low, preferably negative value of $\Delta G°$ is favourable for getting a large equilibrium constant. Since $\Delta G° = \Delta H° - T\Delta S°$, highly negative $\Delta H°$ as well as large and positive $\Delta S°$ values give rise to high K. Large negative $\Delta H°$ means that the system prefers to move to a state of low energy, and the lower the energy of the product molecules, the higher is the equilibrium constant. The same result is also obtained if the product molecules have much larger entropy compared to the reactant molecules. If both these quantities are favourable, a reaction will be both enthalpy-driven and entropy-driven. Thus, the equilibrium state represents a compromise between two opposing tendencies, the tendency for molecules to assume the state of minimum energy and the tendency towards a state of maximum chaos (or entropy)—a conclusion we had come to in our study of thermodynamics (Chapter 9).*

10.5.1 Effects of External Conditions on Equilibria

Let us now explore what effects the variables, pressure and temperature, have on chemical equilibrium. Since in the PCl_5–PCl_3–Cl_2 system, which we have chosen to illustrate the principles of chemical equilibrium, all the species are in the gas phase, we may approximate the concentrations of the species by p/RT terms (since $c = p/RT$ for ideal gases),

$$K_c = \frac{\frac{1}{RT}(p_{PCl_3})_{eq} \frac{1}{RT}(p_{Cl_2})_{eq}}{\frac{1}{RT}(p_{PCl_5})_{eq}} = \frac{1}{RT} \frac{(p_{PCl_3})_{eq}(p_{Cl_2})_{eq}}{(p_{PCl_5})_{eq}} = \frac{1}{RT} K_p$$

The quotient of equilibrium partial pressures is another equilibrium constant, K_p, since RT is constant at a given temperature.† In the present case, $K_p = RTK_c$. The partial pressure of a gas in a mixture of gases is equal to its mole fraction multiplied by the total pressure (Chapter 6). If we replace the partial pressures in the above equation by mole fractions we get,

$$K_c = \frac{\frac{1}{RT}(x_{PCl_3})_{eq} P_{total} \frac{1}{RT}(x_{Cl_2})_{eq} P_{total}}{\frac{1}{RT}(x_{PCl_5})_{eq} P_{total}}$$

$$= \frac{1}{RT} P_{total} \frac{(x_{PCl_3})_{eq}(x_{Cl_2})_{eq}}{(x_{PCl_5})_{eq}}$$

*To illustrate this let us consider three examples: (i) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. Here $CO_2(g)$ has large entropy and this favours the forward reaction (decomposition). However, the decomposition reaction is endothermic and $CaCO_3(s)$ is more stable energywise. The equilibrium pressure of $CO_2(g)$ over $CaCO_3(g)$, therefore, represents the best compromise. (ii) $I_2(g) \rightleftharpoons 2I(g)$. Here again, entropy favours the dissociation to atoms, but energy considerations favour the presence of the bond between atoms. (iii) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$. Here it is difficult to state which direction is favoured by entropy; enthalpy maybe the driving factor.

†In general, we can show that the equilibrium constant, K_c, where concentrations are employed is related to K_p by the relation, $K_p = K_c(RT)^{\Delta n}$ where Δn is the change in the number of mols in the reaction. In the above example $\Delta n = 1$ and $K_p = K_c RT$.

This equation gives a relationship between the equilibrium constant, total pressure and the mole fractions of individual species at equilibrium at a constant temperature.

With the help of the above equation, we can directly see the effect of variation of total pressure. At a given temperature, K is a constant of the system; hence an increase in p_{total} (by decreasing the size of the container) must cause a decrease in the value of $^x P_{Cl_3eq} \, ^x Cl_2eq / ^x P_{Cl_5eq}$. This means that the relative amount of PCl_5 would increase, or the equilibrium will be shifted to the left. Conversely, a decrease in the total pressure of the system (by increasing the volume) will have just the opposite effect; it will shift the equilibrium towards the right. In general, in a gaseous equilibrium reaction, if the total pressure is increased, the equilibrium shifts towards the side with the smaller number of molecules; when the pressure is decreased, the equilibrium shifts towards the side with the large number of molecules. Where the number of molecules is identical on both sides, a change in the pressure will not affect the equilibrium position.

Let us consider other examples to examine the effect of pressure on equilibrium reactions:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_p = \frac{p^2_{NH_3}}{p_{N_2} \, p^3_{H_2}} = \frac{x^2_{NH_3}}{P^2_{total} \, x_{N_2} \, x^3_{H_2}}$$

The formation of ammonia, as is well known, is favoured by pressure since there is a decrease in the number of molecules. Accordingly, we see that the P^2_{total} term is in the denominator of the equilibrium expression; an increase in P_{total} has to be accompanied by an increase in x_{NH_3} to keep K_p constant. The following reaction involving the formation of HI is not affected by pressure since there is no change in the number of molecules. We also see that there is no pressure term in the equilibrium expression.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_p = p^2_{HI}/p_{H_2} \, p_{I_2} = x^2_{HI}/x_{H_2} \, x_{I_2}$$
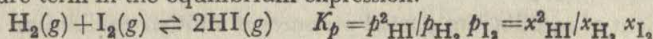
The absolute value of the equilibrium constant of a reaction depends on the manner in which the stoichiometry is expressed. This is understandable since $\Delta G°$ of a reaction is an extensive quantity and $\Delta G° = -RT \ln K$. Let us look at some examples to illustrate this point.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_p(1) = p^2_{HI}/p_{H_2} \, p_{I_2}$$

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \rightleftharpoons HI(g) \qquad K_p(2) = p_{HI}/p^{1/2}_{H_2} \, p^{1/2}_{I_2}$$
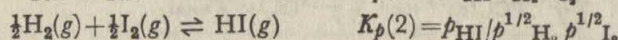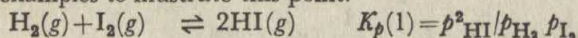
Here, $K_p(1)$ and $K_p(2)$ are not the same and $K_p(1) = [K_p(2)]^2$. While $\Delta G°$ (1) will be twice $\Delta G°(2)$, $\Delta G°$ per mol of HI formed remains constant.

Similarly, for ammonia synthesis,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad K_p(1) = p^2_{NH_3}/p_{N_2} \, p^3_{H_2}$$

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightleftharpoons NH_3 \qquad K_p(2) = p_{NH_3}/p^{1/2}_{N_2} \, p^{3/2}_{H_2}$$
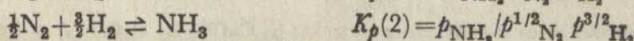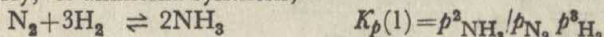
$K_p(1) \neq K_p(2)$ and $K_p(1) = [K_p(2)]^2$. Although $\Delta G°(1) = 2\Delta G°(2)$, we see that $\Delta G°$ per mol of NH_3 formed remains constant. The values of the equilibrium constants for the reverse reactions are reciprocals of the values in the forward direction. For example, the equilibrium constant for the reaction, $HI(g) \rightleftharpoons \tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g)$ is the reciprocal of $K_p(2)$; the $\Delta G°$ for the reverse reaction is the same as the $\Delta G°$ of the forward reaction, but of opposite sign.

We shall now examine the effect of temperature on equilibria. We know that the equilibrium vapour pressure of a liquid increases with temperature and

the magnitude of variation is related to the heat of vapourisation, $\Delta H°_{vap}$ (Chapter 8). Vapourisation is an endothermic process and $\Delta H°_{vap}$ is always a positive quantity. In general, for any equilibrium process, the equilibrium constant increases with temperature if the enthalpy change, $\Delta H°$, associated with that process is positive (endothermic process). The equilibrium constant decreases with temperature if $\Delta H°$ is negative (exothermic process). The quantitative relation between K and $\Delta H°$ can be derived in a simple manner:

$$\Delta G° = -RT\ln K = \Delta H° - T\Delta S°$$

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$$

If $\Delta H°$ and $\Delta S°$ are constants, a plot of $\ln K$ versus $1/T$ should be a straight line with a slope of $-\Delta H°/R$. This is indeed found to be correct. It is convenient to calculate $\Delta H°$ from the values of equilibrium constant at two different temperatures.

$$\ln \frac{K_2}{K_1} = \frac{\Delta H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{or} \quad \log \frac{K_2}{K_1} = \frac{\Delta H°}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where K_2 and K_1 are equilibrium constants at T_2 and T_1 respectively. Here, we have assumed that $\Delta H°$ is constant in the temperature range between T_2 and T_1 $(T_2 > T_1)$. We readily see that $K_2 > K_1$ if $\Delta H°$ is positive, and $K_2 < K_1$ if $\Delta H°$ is negative.

Let us recollect how the equilibrium vapour pressure, p, of a liquid varies with temperature. A plot of $\ln p$ versus $1/T$ is a straight line with a slope of $-\Delta H°_{vap}/R$. Between two temperatures, the variation is given by

$$\log \frac{p_2}{p_1} = \frac{\Delta H°_{vap}}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This equation is similar to that of variation of equilibrium constant with temperature.

We have seen how an equilibrium system reacts to changes in external conditions like pressure and temperature. In both cases, the equilibrium position gets so adjusted as to most effectively utilise the disturbance caused by the change in external conditions. Earlier we had discussed how the equilibrium is shifted when the concentrations of reacting species are changed. Such shifts in equilibrium position caused by changes in conditions are qualitatively, but concisely expressed by *Le Chatelier's principle*. This principle is stated as: *If a change takes place in one of the factors (such as temperature, pressure or concentration) under which an equilibrium exists, the system will tend to adjust itself so as to minimise the effect of that change.* This important generalisation has been verified experimentally in a number of equilibrium systems.

10.5.2 Examples of Equilibrium Systems

Let us first consider a general homogeneous equilibrium reaction,

$$aA + bB \ldots \rightleftharpoons iI + jJ + \ldots$$
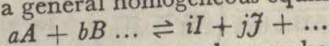
where $a, b, \ldots i, j, \ldots$, etc., represent the number of moles (or molecules) of $A, B, \ldots I, J, \ldots$, etc., taking part in the reaction. The equilibrium constant in terms of concentrations of the reacting species can be represented as

$$K_c = \frac{[I]^i\,[J]^j}{[A]^a\,[B]^b}$$

The change in number of moles in the reaction, $\Delta n = (i+j+\ldots) - (a+b+\ldots)$. The value of K_p of this reaction is then equal to $K_c(RT)^{\Delta n}$.

Consider the gas phase reaction of H_2 and I_2 to form HI.
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
The heat of formation, $\Delta H°_f$, of HI at 25°C is 6.2 kcal mol^{-1}. Since $\Delta H°_f$ of H_2 is zero and that for $I_2(g)$ is 14·9 kcal mol^{-1}, $\Delta H°$ of the reaction at this temperature is equal to $2 \times 6·2 - 14·9 = -2·5$ kcal. The entropies, $S°$, of HI, H_2 and I_2 at this temperature are 49·3, 31·2, and 62·3 eu. $\Delta S°$ of the reaction is, therefore, $(2 \times 49·3) - 31·2 - 62·3 = 5·1$ eu. $\Delta G° = \Delta H° - T\Delta S° = -2500 - 298 \times 5·1 = -4019·8$ cal $= -4·0198$ kcal.
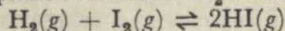
Note that the value of $\Delta G°$ is $-4·0198$ kcal and not $-4·0198$ kcal mol^{-1}; the same is true for $\Delta H°$ and $\Delta S°$. This is because the reaction is for the formation of *two* moles of hydrogen iodide from *one* mole each of hydrogen and iodine.

For this reaction, $K_p = K_c$, since $\Delta n = 0$. We can calculate K from the relation,

$$\log K = -\Delta G°/2·303RT$$

$$K = 10^{-\Delta G°/2.303RT} = 10^{4019.8/2.303 \times 1.98 \times 298}$$

$$= 10^{2·958} = 907·8$$

If we know the initial conditions, we can calculate the exact concentrations of the individual species at equilibrium. For example, if we start with 2 moles of HI, 0·5 mole of H_2 and 0·005 mole of I_2 vapour in a one-litre container at equilibrium, we have,

$$K = 907·8 = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2-x)^2}{\left(0·5 + \dfrac{x}{2}\right)\left(0·005 + \dfrac{x}{2}\right)}$$

On solving the above equation, we get, $x = 0·55$, which means that HI $= 2 - 0·55 = 1·45$ mol litre^{-1}, $H_2 = 0·5 + 0·275 = 0·775$ mol litre^{-1} and $I_2 = 0·005 + 0·275 = 0·28$ mol litre^{-1}.

We can also make some predictions about how the equilibrium constant in this reaction will change with temperature. Since $\Delta H°$ is negative, the reaction is exothermic. Hence, according to Le Chatelier's principle, increase in temperature would favour the formation of the reactants—hydrogen and iodine. Let us calculate the change in the equilibrium constant for a ten-degree rise in temperature. If we take $T_1 = 298$ K, $T_2 = 308$ K, $K_1 = 907·8$, $\Delta H° = -2500$ cal, we obtain the following relation,

$$\log K_2 = \frac{\Delta H°}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \log K_1$$

$$K_2 = 10^{\left(\frac{\Delta H°}{2·303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \log K_1\right)}$$

$$= 10^{\left(\frac{-2500}{2·303 \times 1·98}\left(\frac{1}{298} - \frac{1}{308}\right) + \log 907·8\right)}$$

$$= 10^{2·8992} = 792·9$$

We see that the value of K at 308 K is lower than at 298 K as expected.

Many other interesting examples of homogeneous chemical equilibria can be cited, where all the general principles illustrated above apply. Some familiar equilibria in gas phase are given in Table 10.3 with their characteristic $\Delta H°$, $\Delta S°$, and $\Delta G°$ values at 298·15 K.

Table 10.3 Examples of Homogenous Chemical Equilibria

Reaction	$\Delta H°$ kcal	$\Delta S°$ cal deg^{-1}	$\Delta G°$ kcal	Δn	K
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	13·67	42·00	1·14	1	$\dfrac{[NO_2]^2}{[N_2O_4]} = 0.1450$
$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$	22·04	47·45	7·88	2	$\dfrac{[N_2][H_2]^3}{[NH_3]^2} = 1.6 \times 10^{-6}$
$I_2(g) \rightleftharpoons 2I(g)$	36·15	24·09	28·97	1	$\dfrac{[I]^2}{[I_2]} = 4.4 \times 10^{-22}$
$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$	43·14	5·93	41·38	0	$\dfrac{[NO]^2}{[N_2][O_2]} = 3.6 \times 10^{-31}$
$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2$	21·00	40·70	9·00	1	$\dfrac{[PCl_3][Cl_2]}{[PCl_5]} = 0.151$

A familiar example which nicely illustrates the principle of chemical equilibrium is the acid-catalysed *esterification of a simple carboxylic acid*. Carboxylic acids react with alcohols to give esters and water. These reactions proceed very slowly at room temperature and they can be accelerated by the addition of small amounts of mineral acids. The esterification process is governed by the following equilibrium. A nearly quantitative conversion of the acid to the ester can be achieved by decreasing the concentration of one of the products.

$$R-\overset{\overset{O}{\|}}{C}-OH + R'-OH \underset{}{\overset{H^+}{\rightleftharpoons}} R-\overset{\overset{O}{\|}}{C}-OR' + H_2O$$

$$K = \frac{\left[R-\overset{\overset{O}{\|}}{C}-OR'\right]\left[H_2O\right]}{\left[R-\overset{\overset{O}{\|}}{C}-OH\right]\left[R-OH\right]}$$

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + C_2H_5OH \rightleftharpoons CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + H_2O$$
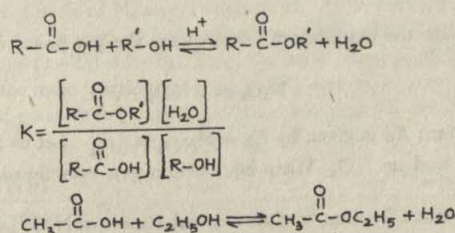
In this case, one can conveniently remove water as and when it is formed and thereby ensure the progress of the reaction in the desired direction. The $\Delta H°$ value of the esterification reaction between acetic acid and ethyl alcohol is nearly zero and therefore temperature has little effect on the equilibrium constant.

Another good example of an equilibrium system from organic chemistry is provided by the reduction of aldehydes and ketones by aluminium alkoxides by the *Meerwin-Pondorff-Virley method*. Most commonly, aluminium isopropoxide is employed for this type of reduction:
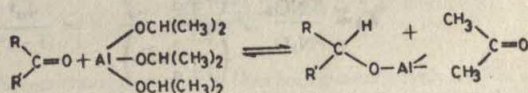
The carbonyl compound to be reduced is heated with aluminium isopropoxide in excess of isopropyl alcohol. The progress of the reaction can be accelerated

by continuously removing one of the products (decreasing the concentration of one of the products). In this case, it is conveniently achieved by distilling away the low boiling acetone (one of the products).

Example 10.6 (a) An alcohol interacts with a ketone by forming a hydrogen bond. (b) Violet coloured iodine forms a brown coloured solution in benzene due to the specific interaction whereby benzene donates electronic charge to iodine. Write equations for the association equilibria in the two cases. Will the equilibrium constants of these reactions increase or decrease with temperature?

Alcohol   Ketone   Hydrogen bonded complex

Benzene   Iodine   Complex
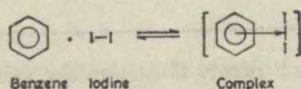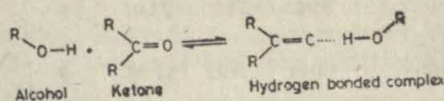
In both cases, we are forming weak bonds between two species. As such, the complex would be energetically more stable. ΔH° for both these reactions would be negative as with all bond-forming reactions. Since ΔH° is negative, the equilibrium constant for association will decrease with increase in temperature (the dissociation constant would increase). ΔH° would also be small (e.g. in the case of hydrogen bonds, we know the energy to be about -5 kcal mol^{-1}) and, therefore, the temperature dependence would not be very appreciable.

Example 10.7 Calculate the equilibrium constant for the gas phase dissociation of nitrogen tetroxide into nitrogen dioxide,

$$N_2O_4 \rightleftharpoons 2 \, NO_2$$
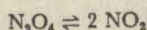
The equilibrium constant K_p is given by $K_p = p^2_{NO_2}/p_{N_2O_4}$. Let us assume that we started with 1 mole of N_2O_4 and no NO_2. When equilibrium gets established, let the total pressure be P atm.

At equilibrium, a certain fraction α, of the original 1 mole of N_2O_4 will be dissociated where α is the degree of dissociation. Since for 1 mole of N_2O_4 dissociated 2 moles of NO_2 are formed, for α mole of N_2O_4, 2α moles of NO_2 will be formed. Thus, at. equilibrium, we have

$$\begin{array}{ccc} N_2O_4 & \rightleftharpoons & 2NO_2 \\ 1-\alpha & & 2\alpha \end{array}$$
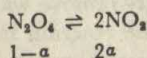
The total number of moles (of N_2O_4 and NO_2 together) will be $1-\alpha+2\alpha=1+\alpha$. Since the partial pressure of a substance is equal to its mole fraction times the total pressure,

$$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha}P \quad \text{and} \quad p\,NO_2 = \frac{2\alpha}{1+\alpha}P$$

The equilibrium constant expression can be written as

$$K_p = \frac{p^2 NO_2}{p_{N_2O_4}} = \frac{\left(\dfrac{2\alpha}{1+\alpha}P\right)^2}{\left(\dfrac{1-\alpha}{1+\alpha}P\right)} = \frac{4\alpha^2}{(1-\alpha^2)}P$$

Experimentally, the fraction dissociated or the degree of dissociation, α, can be easily determined if the equilibrium composition in terms of number of moles of $NO_2(2\alpha)$ or N_2O_4 $(1-\alpha)$ is known. Once α and P are known, K_p is readily calculated.

Example 10.8 At 35°C, the value of K_p for the above equilibrium [Example 10.7] is 0·3174. Calculate the degree of dissociation α when P is 0·2382 atm.

$$K_p = 0·3174 = \frac{4\alpha^2}{1-\alpha^2} P = \frac{4\alpha^2}{1-\alpha^2} (0·2382)$$

Since α is small, we can neglect α^2 in comparison with unity. We then have,

$$4\alpha^2 = \frac{0·3174}{0·2382} \text{ or } \alpha = \left(\frac{0·3174}{0·2382 \times 4}\right)^{1/2} = 0·5768$$

i.e. we should expect 57·68 per cent dissociation.

Example 10.9 In this example we shall carry out equilibrium calculations on the formation of ammonia from nitrogen and hydrogen:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
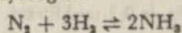
This will have an equilibrium constant, $K_p(1) = \dfrac{p^2_{NH_3}}{p_{H_2} \cdot p^3_{H_2}}$

If the equilibrium reaction is written as, $(1/2)N_2 + (3/2)H_2 \rightleftharpoons NH_3$, the equilibrium constant is given by

$$Kp (2) = \frac{p_{NH_3}}{p^{1/2}_{N_2} p^{3/3}_{H_2}}$$

When calculating equilibrium compositions, we should employ the stoichiometry of the reaction that is used in obtaining K_p. The equilibrium constant K_p (for the formation of 2 moles of NH_3) has a value of $7·08 \times 10^{-4}$ at 350°C. Let the pressure be 10 atm.

Suppose we start with 1 mole of N_2 and 3 moles of H_2. At equilibrium, let x mole of N_2 and hence $3x$ moles of hydrogen be used up in forming $2x$ moles of NH_3. The total number of moles will be $(1-x) + (3-3x) + (0+2x) = 4-2x$. Thus, the mole fraction of N_2 at equilibrium will be $(1-x)/(4-2x)$ and the mole fractions of H_2 and NH_3 will be $(3-3x)/(4-2x)$ and $2x/4-2x$ respectively. If the total pressure is P, the equilibrium constant K_p can be written as

$$K_p = \frac{p^2_{NH_3}}{p_{N_2} p^3_{H_2}} = \frac{\left(\dfrac{2x}{4-2x} P\right)^2}{\left(\dfrac{1-x}{4-2x} P\right)\left(\dfrac{3-3x}{4-2x} P\right)^3} = \frac{16x^2 (2-x)^2}{27P^2(1-x)^4}$$

We know that the value of x is less than unity and therefore the above equation approximates as

$$K_p = \frac{16x^2(4)}{27P^2} = \frac{64x^2}{27P^2}$$

For $K_p = 7·08 \times 10^{-4}$ and $P = 10$ atm

$$x^2 = \frac{27P^2 K_p}{64} = \frac{27 \times 10^2 \times 7·08 \times 10^{-4}}{64} \text{ or } x = 0·173$$

Number of moles of NH_3 at equilibrium is $2x$ out of total number of $4-2x$ moles. Thus, mole percentage of ammonia

$$= \frac{2(0·173)}{4-2(0·173)} \times 100 = 7·4$$

Example 10.10 The reaction shown overleaf has been quantitatively studied at 20°C in a solution of 96 per cent ethyl alcohol, and the value of $\Delta G°$ has been found to be $-2·7$ kcal. Calculate the composition at equilibrium assuming that initially we had no aldehyde and hydrogen cyanide, but only the cyanohydrin with a concentration of 7·35 g in 500 ml of the solution.

para-Methylbenzal-
dehyde

para-Methylbenzaldehyde-
cyanohydrin
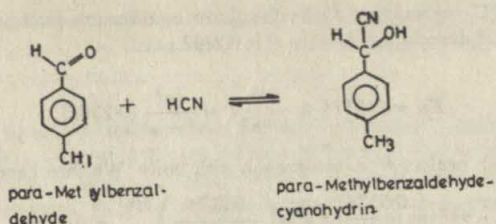
The molecular formula of the cyanohydrin is C_9H_9ON, hence the molecular mass is $(9 \times 12)+(9 \times 1)+(1 \times 16)+(1 \times 14)=147$. Since, initially, there were 7·35 g of cyanohydrin in 500 ml of the solution, 1 litre of the solution will contain 14·7 g. Molecular mass being 147, the initial concentration of cyanohydrin is 0·1 mol litre^{-1}.

$$\Delta G^\circ = -RT \ln K = -2 \cdot 303 \, RT \log K$$

$$K = 10^{\dfrac{\Delta G^\circ}{2.303 \, RT}} = 10^{\dfrac{2.700}{2.303 \times 1.98 \times 293}} = 10^{2.02}$$

$$K = \frac{[\text{cyanohydrin}]}{[\text{aldehyde}] \, [\text{HCN}]} = \frac{0 \cdot 1(1-\alpha)}{(0 \cdot 1\alpha)^2}$$

where α is the fraction of products formed from each mole of the cyanohydrin at equilibrium:

$$10^{2 \cdot 02} = 104 \cdot 7 = \frac{0 \cdot 1(1-\alpha)}{(0 \cdot 1\alpha)^2}$$

$$\alpha = 0 \cdot 309$$

Therefore, [cyanohydrin] $= 0 \cdot 1(1-0 \cdot 309) = 0 \cdot 0691$ mol litre^{-1}
and [aldehyde] $=$ [HCN] $= 0 \cdot 0309$ mol litre^{-1}

10.6 HETEROGENEOUS EQUILIBRIA

All the equilibrium systems we discussed in the previous sections were in homogeneous media. We shall now consider a multi-phase system as an example of *heterogeneous equilibria*. A common example of such a system is provided by the decomposition of solid $CaCO_3$ into solid CaO and gaseous CO_2:
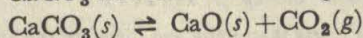
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The equilibrium constant for this reaction can be written as

$$K' = \frac{[CaO(s)] \, [CO_2(g)]}{[CaCO_3(s)]}$$

We see that the equilibrium constant expression involves two pure solids, $CaCO_3$ and CaO. It is costomary not to include the concentrations of pure solids in equilibrium expressions, since they do not change due to chemical reaction. Further, the quantity of $CaCO_3$ or CaO does not affect the partial pressure of CO_2. The 'concentrations' of pure solids are thus included in the equilibrium constant itself. In the case of the decomposition of $CaCO_3$, the equilibrium expression is written as

$$K'' = K'[CaCO_3]/[CaO] = [CO_2]$$

replacing $[CO_2]$ by the partial pressure of CO_2, $K = p_{CO_2}$.

The equilibrium constant for this reaction is thus given by the equilibrium pressure of CO_2. K (as well as p_{CO_2}) has a constant value at a given temperature.

This means that at every temperature there is a fixed value of the pressure of CO_2, which is called the *dissociation pressure*. The variation K with temperature is given by the variation of p_{CO_2} with temperature.

For the dissociation of the salt hydrate,

$$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(g)$$
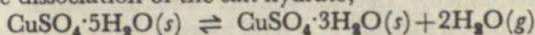
the equilibrium constant is given by $K = p^2_{H_2O}$.

For the dissociation of the metal complex $AgCl \cdot 3NH_3$,

$$2(AgCl \cdot 3NH_3) \rightleftharpoons 2AgCl + 6NH_3$$
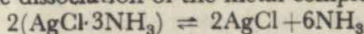
$$K = p^3_{NH_3}$$

For the decomposition of the oxide Ag_2O,

$$2Ag_2O(s) \rightleftharpoons 4Ag(s) + O_2(g)$$
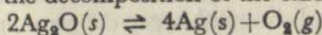
$$K = p_{O_2}$$

Example 10.11 Dissociation pressure of CO_2 at 500°C is 0·773 mm. At this temperature, $\Delta H°$ of the reaction is 43·2 kcal mol⁻¹. Calculate the dissociation pressure at 600°C assuming that $\Delta H°$ remains constant in this temperature range.

$$\log \frac{K_2}{K_1} = \frac{\Delta H°}{2 \cdot 303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Since $K = p_{CO_2}$, we can rewrite the above equation as

$$\log \frac{p_{CO_2}(T_2)}{p_{CO_2}(T_1)} = \frac{\Delta H°}{2 \cdot 303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

or,

$$\log \frac{p_{CO_2}(873 \text{ K})}{0 \cdot 773} = \frac{43200}{2 \cdot 303 \times 1 \cdot 98} \left(\frac{100}{773 \times 873} \right)$$

Therefore, p_{CO_2} at 873 K = 19·6 mm.

Example 10.12 A solid oxide of the formula MO_2 loses slight amounts of oxygen at high temperatures. Employing the law of mass action indicate the nature of equilibrium involved and show how the electrical conductivity of the oxide should vary with the partial pressure of oxygen. Can you comment on the type of semiconduction in this oxide?

Since the oxide loses oxygen, the equilibrium relation can be written as

$$O^{2-} \rightleftharpoons \tfrac{1}{2} O_2(g) + 2e + \text{oxide ion vacancy}$$
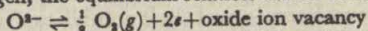
where e stands for the electron freed in the process. The equilibrium constant of this reaction is given by,

$$K = (V_O) \ (e)^2 \ p^{1/2}_{O_2} \quad \text{where } V_O = \text{oxide vacancy}.$$

Since $(V_O) = 2(e)$, we have $K = 2(e)^3 \ p^{1/2}_{O_2}$ and hence $(e)^3 = K' \ p^{-1/2}_{O_2}$ where $K' = K/2$.

Therefore (e) is proportional to $p^{-1/6}_{O_2}$. Since the conductivity is proportional to (e), it would also vary with oxygen pressure in $p^{-1/6}_{O_2}$ manner.

The oxide is a n type semiconductor since electrons are available for conduction.

We can similarly work out the case of an oxide with oxygen excess (p type semiconductor) where the conductivity would increase with oxygen partial pressure, i.e. $(e) \propto p^{1/n}_{O_2}$.

10.7 SOLUBILITY EQUILIBRIA

A common example of heterogeneous equilibrium is the dissolution of one substance in another to form a homogeneous one-phase system. The solute (substance that dissolves) may or may not be in the same state as the solvent. The factors that govern solubility are again related to free energy. In general,

if the free energy of interaction of the solute and the solvent is negative, solution will be obtained. If the ΔG value is greater than zero, the solute and solvent will exist as two separate phases. When the free energy of interaction is zero, an equilibrium is established. Let us consider some examples. All gases mix freely together, so that a mixture of several gases is still in a homogeneous phase. We may then say that all gases dissolve in each other in all proportions yielding a homogeneous single-phase solution. This is an example of a homogeneous equilibrium process and the partial pressure of each gas is given by Dalton's law ($p_a = a P_{total}$).

Let us consider the case of a solid that dissolves in water. When cane sugar is added to water at 298 K, about 200 g of the solid sugar dissolves in 100 g water to from a homogeneus solution. Further addition of sugar leads to no further dissolution and the sugar remains as a solid precipitate in contact with the liquid. Such a solution is termed as *saturated* and at that temperature, it will take in no more of the solid. We may view this situation as an equilibrium process. Until saturation is reached, the free energy of interaction between sugar and water is negative, causing more sugar to dissolve in water. At the saturation point, the free energy of interaction between sugar and water matches exactly the free energy of solute-solute as well as solvent-solvent interaction. A dynamic equilibrium is achieved, where the net number of solute molecules in solution is constant at constant temperature. If we were to change the temperature of the system, the amount of solute in the solution can be made to vary.

If the heat of solution of a solute in a solvent is endothermic (i.e. heat is absorbed when solution is formed), then according to Le Chatelier's principle one expects the solubility of the solute in the solvent to increase with temperature. Conversely, if heat is liberated when solution is formed (heat of solution is exothermic), one expects the solubility to decrease with an increase in temperature. The solubility of sugar in water is known to increase with increasing temperature (Fig. 10.9a). Thus, in this case, the heat of solution is endothermic. Benzoic acid and potassium nitrate are other examples of solutes whose heats of solution in water are endothermic. On the other hand, lithium sulphate, lithium carbonate and manganese sulphate are examples of solutes whose heats of solution in water are exothermic and their solubilities in water decrease with rise in temperature (Fig. 10.9a).
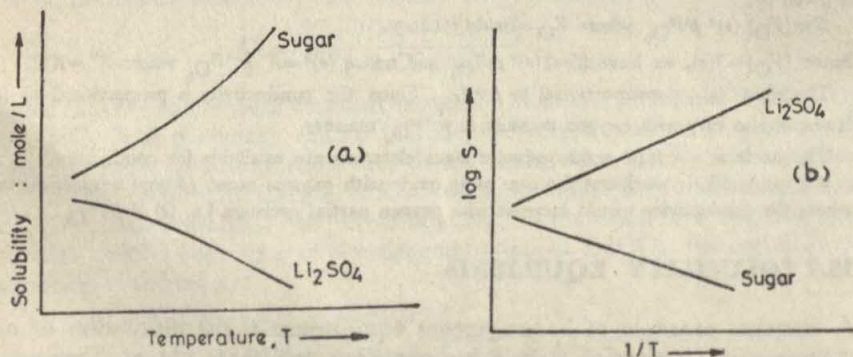
Fig. 10.9 The dependence of the solubility of solutes on temperature: (a) plot of solubility against temperature and (b) plot of logarithm of solubility against inverse temperature.

We may quantify the above ideas on the temperature-dependence of solubilities. Consider the case of a saturated solution of KNO_3 in water, in contact with solid KNO_3. The equilibrium may be represented as,

$$KNO_3(s) \rightleftharpoons KNO_3 \ (in \ solution)$$

$$K' = \frac{[KNO_3 \ (in \ solution)]}{[KNO_3(s)]}$$
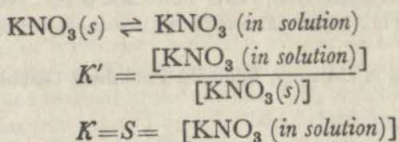
$$K = S = [KNO_3 \ (in \ solution)]$$

The equilibrium constant K is a constant at a given temperature. The denominator in K' is simply the concentration of solid KNO_3 and hence, K is simply the concentration of the salt in solution, S. Hence, the variation of solubility with temperature is given by the equation,

$$\log \frac{K_2}{K_1} = \log \frac{S_2}{S_1} = \frac{\Delta H^\circ}{2 \cdot 303 R}\left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where S_1 and S_2 are the solubilities in mol litre^{-1} at temperatures T_1 and T_2, ΔH° the standard state heat of solution, and R the gas constant. A plot of $\log S$ versus $1/T$ will thus yield a straight line (Fig. 10.9b), whose slope would give us $\Delta H^\circ/2 \cdot 303 R$. If ΔH° is negative (exothermic), $S_2 < S_1$ and if ΔH° is positive (endothermic), $S_2 > S_1$.

As we had mentioned earlier, the solubility of a solute in a solvent is governed by the free energy of interaction between the two. The reason why inorganic salts dissolve in water is that the energy of attractive interaction between the charged salt ions and the water dipole favours dissolution. Likewise, sugar can form hydrogen bonds with water leading to an energetically favoured solution state. If we now take the case of kerosene or hydrocarbons and water, there are no significant preferential attractive forces between the solute hydrocarbon and solvent water. A hydrocarbon molecule has approximately the same energy of interaction with either water, or another hydrocarbon molecule. Thus, it is more or less indifferent about dissolving in water. On the other hand, for solvent water to interact with the hydrocarbon, it has to sacrifice attractive hydrogen bonding forces that it may otherwise experience with other water molecules leading to an unfavourable situation. It is partly because of this reason that hydrocarbons do not dissolve in water and are termed *hydrophobic*, i.e. water repelling.

An interesting application of solubility equilibria occurs with *detergents*. Consider a substance like soap. *Soaps* are salts of long chain fatty (organic) acids. Thus, a soap molecule contains at one end an ionic part that would interact favourably with water (*hydrophilic* or water-loving) and cause the soap molecules to dissolve. However, the long paraffin chain part (tail) of the soap molecule would behave like an oil (*hydrophobic*) and oppose solubility. As a result, soap dissolves in water only to a limited extent. Even in this limited amount, soap molecules tend to associate in water solution, in such a fashion that all the hydrocarbon tail parts come together to form the 'interior' and the salt, or ionic part, is exposed to the solvent. Such an aggregation of amphiphilic substances is called a *micelle* and is important in the mechanism of the cleansing action of soaps.

SUGGESTED READING

D. Dreisbach, *Liquids and Solutions*, Haughton-Mufflin Co., Boston, Mass., 1966.

A. Findlay, *The Phase Rule and its Applications*, Dover Publications Inc., New York, 1951.

J. H. Hildebrand, *An Introduction to Molecular Kinetic Theory*, Reinhold Publishing Corporation, New York, 1963.

W. F. Kieffer, *The Mole Concept in Chemistry*, Reinhold Publishing Corporation, New York, 1963.

PROBLEMS

10.1 How many phases are present in the following systems?

(*a*) A finely ground mixture of graphite, sulphur and sodium nitrate.

(*b*) A mixture of graphite and diamond powder.

(*c*) A mixture of the following gases with their partial pressures given in parentheses: H_2(50 mm), SO_2 (230 mm), N_2(175 mm), Xe(5 mm), NO(300 mm).

(*d*) An aqueous solution saturated with NaCl and KCl in contact with excess NaCl.

(*e*) An iceberg floating on clear sea water in presence of clean air.

10.2 What are the number of components in the following systems?

(*i*) A mixture of molten lead, tin and bismuth.

(*ii*) (*a*) Nitrogen and oxygen at 25°C. (*b*) This gas mixture heated to 1000°C.

(*iii*) $CaCO_3$ in a closed container with air removed from it.

(*iv*) A sample of atmospheric air: N_2 (78·03% by volume), O_2(20·99%), Ar (0·94%), CO_2 (0·023 %), H_2(0·01%), Ne (0·0015%), He (0·0005%), Kr (0·00011%), Xe (0·000009%), H_2O (0·004881%).

(*v*) Two ice cubes floating on water in a closed container in presence of water vapour.

10.3 What are the number of degrees of freedom in the following systems?

(*a*) Solid ice I, II, III in equilibrium.

(*b*) Liquid helium I in equilibrium with helium gas at 60 K.

(*c*) Water boiling to form steam.

(*d*) Liquid carbon in equilibrium with carbon vapour at 6000 K.

10.4 (*a*) Camphor ($C_{10}H_{16}O$) sublimes when heated at atmospheric pressure. From this fact what information can you derive about the camphor phase diagram?

(*b*) Hail is solid ice formed in upper atmosphere. With the help of the water phase diagram suggest conditions prevailing in upper atmosphere when hail formation takes place.

10.5 Two blocks of ice are brought in contact and pressed together. After releasing the pressure, they join to form one large block of ice. Will the same thing happen in the case of solid carbon dioxide? Explain your answer.

10.6 The molar boiling point elevation constant of carbon tetrachloride is 5·03 deg molal^{-1}. The normal boiling point of carbon tetrachloride is 76·8°C. At what temperature will a carbon tetrachloride solution containing a solute of molecular mass 226 boil if the solution contains 5 per cent solute by weight?

10.7 What is the boiling point of a 10·0 per cent (by weight) solution of camphor in benzene and in methanol?

10.8 The normal freezing point of nitrobenzene ($C_6H_5NO_2$) is 5·82°C. A 0·25 molal solution of a certain solute in nitrobenzene causes a freezing point depression of 2°C. Calculate the value of K_f for nitrobenzene.

10.9 0·05 g of an organic substance was dissolved in 5·00 g of camphor and the solid solution melted at 173·8°C. What is the molecular mass of the substance?

10.10 A dilute aqueous solution has a freezing point of −0·0372°C. What is its osmotic pressure at 25°C?

10.11 For the polymer solution described in Example 10·4 of the text, calculate the elevation in the boiling point and depression of the freezing point. Based on these data, which method will you recommend for the determination of the molecular mass of the polymer?

10.12 In an experiment starting with 1 mole of ethyl alcohol, 1 mole of acetic acid and 1 mole of water at 100°C, the equilibrium mixture on analysis shows that 54·3 per cent of the acid is esterified. Calculate the equilibrium constant of this reaction.

10.13 The equilibrium constant of the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is $K_p = 10^{-5}$ at 8°C. If a solution containing 0·25 mole of N_2O_4 in 100 ml chloroform is prepared, what will be the concentration of N_2O_4 and NO_2 when equilibrium is reached?

10.14 The value of K_p for the reaction $I_2(g) \rightleftharpoons 2I(g)$ is 0·014 at 800°C. If ϵ_{I-I} is 35·6 kcal, calculate the value of K_p at 900°C.

10.15 In the hydrogenation reaction forming ethane from ethylene $C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$, if the initial pressure of C_2H_4 is 1 atm and that of H_2 is 2 atm, what will be the equilibrium composition at 25°C?

$$\Delta G^\circ_{f298} \ C_2H_4(g) \rightleftharpoons 16·282 \text{ kcal mol}^{-1}$$
$$\Delta G^\circ_{f298} \ C_2H_6(g) \rightleftharpoons 30·989 \text{ kcal mol}^{-1}$$

How long will it take to reach the equilibrium condition?

11

Equilibrium-II : Acids, Bases and Salts
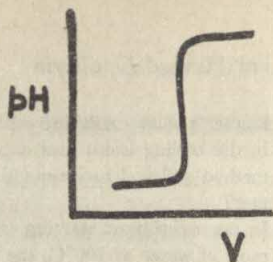
There is nothing in the Universe but alkali and acid, from which Nature composes all things.

O. TACHENIUS

' *Need Two, from you–Have Pair, will share'*

C. A. VANDERWERF

We have already developed the general principles of chemical equilibrium and applied them mainly to understand chemical reactions in gas phase. A large number of chemical reactions in the laboratory, industry as well as in biological systems take place in the liquid phase, especially in aqueous medium, where many inorganic (and some organic) compounds would be present as ions. Now, we shall discuss some aspects of chemical equilibria involving ions.

11.1 SOLUTIONS OF IONS

We have seen in Chapter 4 that the ion-pair molecule Na^+-Cl^- is formed in the vapour phase because of the attractive coulomb force between the oppositely charged ions. The energy for such a coulombic attraction is given by $-e^2/r$ where e is the electronic charge and r is the distance between Na^+ and Cl^-; here we have assumed that the interaction is between two unit charges in vacuum. A more general expression for the potential energy for coulombic interaction between two ions is given by,

$$V = -Z_1 Z_2 e^2/Dr$$

where Z_1 and Z_2 are the charges on species 1 and 2 and D is the dielectric constant of the medium in which the ions are present. In air, $D=1$ and the energy of coulomb attraction between Na^+ and Cl^- at a distance of 2.8 A (NaCl lattice distance) turns out to be -119 kcal mol^{-1}. This means that the attractive interaction between Na^+ ion and the neighbouring Cl^- ion is quite large in solid NaCl. When we dissolve solid NaCl in a solvent, the

coulombic or ionic interaction will be modified to a great extent by the dielectric constant of the solvent medium. In dioxane, where the dielectric constant is about $2 \cdot 2$, the attraction energy between Na^+ and Cl^- would be -52 kcal mol^{-1}, about half as in vacuum or air. The two ions will still be ' held ' in contact in dioxane as ' *ion-pair* ' or *ion multiplets*. In water $(D=80)$ the attraction energy reduces to $-1 \cdot 5$ kcal mol^{-1}, while in the solvent formamide, it is only about $-0 \cdot 8$ kcal mol^{-1}. Thus in water or in formamide, Na^+ does not ' hold on ' to the Cl^- with any great strength, but exists free of the latter's influence.

In water and similar polar solvents, another factor of importance is the interaction between the ion and the solvent molecules. Water molecule is a good dipole (dipole moment $1 \cdot 8$ debye). *Ion-dipole* forces between Na^+ and H_2O, and also between Cl^- and H_2O are significantly greater than $-1 \cdot 5$ kcal mol^{-1}. Consequently, NaCl will exist in water not as Na^+Cl^-, as in vacuum or dioxane, but as $Na^+...(H_2O)_n$ and as $Cl^-...(H_2O)_m$. Each ion is surrounded by several molecules of the solvent which lower the energy even more than the ion-pairing energy. Dissolution of common salt (NaCl) in a solvent has the effect of reducing the force between the ions and consequently ion separation increases with increase in the dielectric constant or the polarity of the solvent.

$$Na^+Cl^-(s) + H_2O \rightarrow Na^+(H_2O)_n + Cl^-(H_2O)_m$$
$$\text{or} \quad Na^+Cl^-(s) + H_2O \rightarrow Na^+(aq) + Cl^-(aq)$$
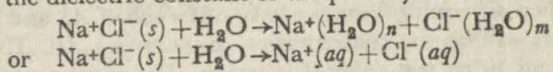
This process is known as *ion solvation*.* In water, sodium ions will behave as solvated ions that are not greatly influenced by the presence of the (solvated) chloride ions. If one passes an electric current through an aqueous solution of NaCl, conduction of electricity results. The conductivity of NaCl in dioxane solution is far less than that in water. In dioxane, the binding energy of Na^+ and Cl^- is considerable and the ion-pair Na^+Cl^- will, in effect, be predominantly a neutral species. This gives rise to the operational definition of an *electrolyte*. We define an electrolyte as a compound that conducts electricity in a medium. (Note the importance of the medium.) A given compound may conduct electricity in water but may not conduct to the same extent in another solvent medium. Historically, the concept of an electrolyte arose with reference to aqueous solutions, and when we talk of a substance as an electrolyte, we usually assume that it is in aqueous medium.

Compounds that are ionic, or predominantly ionic, behave as electrolytes in water. Similarly compounds where the bonding is covalent are poor conductors. In aqueous solution, separation into ions does not occur for covalent compounds and so these do not behave as electrolytes. Molecules of sucrose $(C_{12}H_{22}O_{11})$ or benzene are, therefore, not electrolytes. All salts, being predominantly ionic in character, are electrolytes. However, many compounds like HCl, even though they possess significant covalent character, become electrolytes in water since solute-solvent interactions favour ionisation and ion separation.

We are now in a position to state the factors that govern electrolyte behaviour: the nature of bonding in the compound, the strength of the coulombic interaction between the oppositely charged ions in the molecules, the solvent medium, and the interaction between the solute ions and the solvent. Besides these, the concentration of the solute in the solvent is also important. In many instances

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*The symbol (aq) means that the species is solvated by water molecules. The exact number of water molecules is not specified here.

Table 11.1 Ionisation of Acetic Acid in Water

Concentration	*% Ionisation*	*Concentration*	*% Ionisation*
1·0 *M*	0·4	0·001 *M*	15·0
0·1 *M*	1·3	0·00001 *M*	75·0
0·01 *M*	4·3		

the extent of ionisation of an electrolyte increases as the concentration decreases. That is, the more dilute a solution, the greater is the extent to which it ionises. Table 11.1 shows the variation of ionisation with concentration of acetic acid, CH_3COOH, in water solutions. In these cases, one may visualise the molecule as involved in an equilibrium with the ions. In general, such an equilibrium may be written as:

$$AB \rightleftharpoons A^+ + B^-$$

$$K_{ionisation} = \frac{[A^+][B^-]}{[AB]}$$
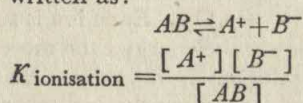
If the concentration of *AB* were intially $1M$, and if some fraction of this, say α were to ionise, then at equilibrium, we have αM each of A^+ and B^- and the rest, i.e. $(1-\alpha)M$, will be the concentration of unionised *AB*. The quantity, α is usually referred to as the *degree of ionisation*. The more general name for α is *degree of dissociation*, a term that we have encountered in the last chapter. Thus,

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{\alpha \cdot \alpha}{(1-\alpha)} = \frac{\alpha^2}{1-\alpha}$$

A typical value for the ionisation constant, K, of a weak electrolyte like acetic acid is 10^{-5}. Most inorganic salts ionise completely in water and in these cases, $\alpha = 1$ or $K = \infty$. Substances with large values of K (greater than $10-10^2$) are called strong electrolytes while those with small values of K (<1) are called weak electrolytes.*

11.2 IONIC EQUATIONS AND SOLUBILITY

In dilute solution of an electrolyte, the constituent ions are essentially independent of one another. Thus, in a solution of NaCl and KNO_3, the four ions Na^+, Cl^-, K^+ and NO^-_3 are uniformly distributed throughout the solution. To represent reactions occurring between ions, we write the ions as separate entities. For example, when a solution of $BaCl_2$ is treated with a solution of Na_2SO_4, a precipitate of $BaSO_4$ results. The equation is written as

$$Na_2SO_4 + nH_2O \rightarrow 2\,Na^+(aq) + SO_4^{2-}(aq)$$
$$BaCl_2 + nH_2O \rightarrow Ba^{2+}(aq) + 2Cl^-(aq)$$
$$2\,Na^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2\,Cl^-(aq) \rightarrow$$
$$2\,Na^+(aq) + 2Cl^-(aq) + BaSO_4(solid)$$
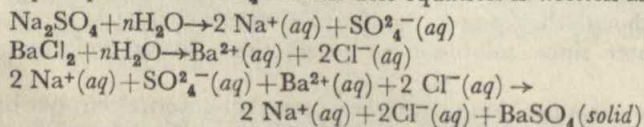
Since Na^+ and Cl^- are unchanged, the net ionic equation will be
$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$
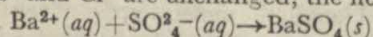
*It is worthwhile to emphasise here the idea of charge balance. In all ionisation phenomena, the total number as well as the signs of charges are conserved. One cannot generate a single charge out of nothing. This is another basic conservation law, similar to the law of conservation of matter (mass or energy).

The same ionic equation will result, i.e. $BaSO_4$ will precipitate out of solution, even if we use K_2SO_4 and $BaCl_2$, or Li_2SO_4 and $Ba(NO_3)_2$. The reaction leading to the precipitation thus involves only Ba^{2+} and SO^{2-}_4 and not the other ions. Notice that the law of charge conservation is valid in all the examples.

Another equilibrium property of electrolyte solutions is their solubility. A salt like NaCl dissolves in water because the energies of dissolution of Na^+ and of Cl^- are favourable. In a different solvent, the interaction between the electrolyte and the solvent may not be sufficiently strong. In such a case, the tendency to solvate the ions and to separate them from one another will be less and the electrolyte does not find it energetically favourable to dissolve. This is the reason why common salt does not dissolve in benzene. The solvation energy of sodium and chloride ions in benzene is not sufficient to overcome the coulombic attraction energy between the Na^+ and Cl^- in solid sodium chloride.

Under appropriate conditions of temperature, pressure and electrolyte concentration, the energies of solvation and of precipitation may be equal. Then an equilibrium is established between dissolution and crystallisation. If we take a saturated solution of, say, sodium chloride, an equilibrium relation may be written as

$$nH_2O + NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$
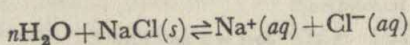
Increasing the amount of water will, by Le Chatelier's principle, drive the system towards right and more salt will dissolve. Addition of Cl^- (or Na^+) will send the system towards left and more salt will crystallise out of solution. The latter is an example of what is called the common ion effect which we will discuss later. Temperature is another factor that affects solubility (see Chapter 10). When potassium bromide is dissolved in water, heat is absorbed (endothermic process); conversely when KBr crystallises out of water, heat is liberated (exothermic process). Consequently, the solubility of potassium bromide in water will increase with an increase in the temperature of the system. The dissolution of most ionic substances in water is an endothermic process and their solubilities, therefore, increase with temperature.

We can define yet another equilibrium constant, termed the *solubility product*. For example, for the equilibrium involving solid Na^+Cl^-, and sodium and chloride ions in solution, we can write,

$$K = \frac{[Na^+(aq)]\ [Cl^-(aq)]}{[H_2O]^n\ [NaCl(s)]}$$

Here, the change in the water concentration is negligible or, $[H_2O]^n$ is constant. Similarly, the concentration of NaCl(s) does not change in the solid phase. We can, therefore, rewrite the above expression for the equilibrium constant as

$$K_{sp} = [Na^+(aq)]\ [Cl^-(aq)]$$

where K_{sp} is an equilibrium constant, being a product of the concentrations of the anion and of the cation in solution (in equilibrium with the solid salt). K_{sp} is given the name *solubility product* since it is a measure of the solubility of the ions from the solid. In a general case, we may write,

$$AB(s) + \text{water} \rightleftharpoons A^+(aq) + B^-(aq)$$
$$K_{sp} = [A^+(aq)]\ [B^-(aq)]$$
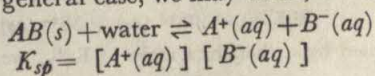
Table 11.2* lists the solubility products of some substances.

*When expressed thermodynamically, K_{sp} or any such constants of equilibrium are dimensionless. This is why K_{sp} is usually expressed as a number.

Table 11.2 Solubility Products in Water of Some Salts at 25°C

Compound	K_{sp}	Compound	K_{sp}
AgCl	1.8×10^{-10}	BaF_2	1.7×10^{-6}
AgI	8.5×10^{-17}	CaF_2	1.7×10^{-10}
$BaSO_4$	1.1×10^{-10}	$Al(OH)_3$	1.4×10^{-34}

From Table 11.2, we see that AgCl dissolves more in water than AgI. In general, a low value of K_{sp} for a salt means that the solubility of the salt is low, but K_{sp} itself is not proportional to the solubility of the salt. In this sense, the name solubility product is rather misleading. However, it is possible to calculate the solubility of a salt if the value of K_{sp} is known and vice versa.

Example 11.1 Using Table 11·2, determine the amount of silver chloride that dissolves in water.

$$K_{sp} \equiv [Ag^+ (aq)] [Cl^- (aq)] = 1.8 \times 10^{-10}$$

One mol of AgCl contains 1 mol of silver and one mol of chloride ions, and since there is on other source for these ions in solution,

$$[Ag^+(aq)] = [Cl^-(aq)] = x \text{ mol litre}^{-1}$$

Hence,

$$K_{sp} \text{ (AgCl)} = 1.8 \times 10^{-10} = x^2$$

$$x = 1.3 \times 10^{-5} \text{ mol litre}^{-1}$$

Since 1 mol of Ag^+ comes from 1 mol of AgCl, the concentration of AgCl in solution is also the same. In other words, the solubility of AgCl in water at 25°C is 1.3×10^{-5} mol litre^{-1}.

In general, for electrolytes that yield only two ions (i.e. binary electrolytes), the solubility is given (in mol litre^{-1}) by the square root of the solubility product. This simple relation becomes a little complex when a salt yields two ions, each with different charge.

Example 11.2 The solubility product of CaF_2 in water at 18°C is 3.45×10^{-11}. Calculate the solubility.

$$CaF_2 (s) \rightleftharpoons Ca^{2+}(aq) + 2 F^- (aq)$$
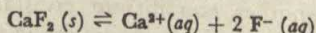
For each ion of Ca^{2+} produced, there are two F^- ions present. And 1 mol of CaF_2 produces 1 mol of Ca^{2+} and 2 moles of F^-. Thus, if the concentration in solution (solubility) of CaF_2 is xM, $Ca^{2+} (aq) = xM$ and $F^- (aq) = 2xM$.

$$K_{sp} \text{ (CaF}_2\text{)} = [Ca^{2+}(aq)] [F^-(aq)]^2$$

$$= x \cdot (2x)^2$$

$$= 4x^3 = 3.45 \times 10^{-11}$$

Solving for x, $x = 2.05 \times 10^{-4} M$, or the solubility of CaF_2 in water at 18°C is 2.05×10^{-4} mol litre^{-1}.

Example 11.3 Bismuth sulphide dissolves in water, at 20°C, to the extent of 1.7×10^{-15} mol litre^{-1}. Calculate the value of K_{sp}.

The formula of bismuth sulphide is Bi_2S_3. The solubility equilibrium in water is

$$Bi_2S_3(s) \rightleftharpoons 2Bi^{3+} (aq) + 3S^{2-} (aq)$$
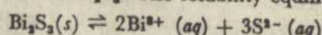
If the solubility is denoted by x, then for x moles of Bi_2S_3, we have $2x$ moles of Bi^{3+} and $3x$ moles of S^{2-}.

$$K_{sp} = [Bi^{3+} (aq)]^2 [S^{2-} (aq)]^3$$

$$= (2x)^2 (3x)^3 = 108x^5$$

$$= 108 \times (1.7 \times 10^{-15})^5 = 1.5 \times 10^{-72}$$

The effect of temperature on solubility product is the same as on solubility. In general solubilities of salts increase with increasing temperature, and so does K_{sp}. For example, the K_{sp} value of $PbCl_2$ is 1.5×10^{-4} at 20°C, 12×10^{-4} at 60°C, and 40×10^{-4} at 90°C.

11.3 THE COMMON ION EFFECT

The solubility product, as we have seen above, is a modified equilibrium constant. Any change in the conditions of solubility equilibrium, as Le Chatelier states, will be resisted by the system. Another way of stating this is as follows: since at a given temperature, K_{sp} is constant, change in any other variable will cause a change in the solubility of the salt. To illustrate this, let us take the case of silver chloride. This sparingly soluble salt has a K_{sp} value of 1.8×10^{-10} in water at 25°C. This means that the solubility of AgCl is $1.3 \times 10^{-5} M$. This quantity of AgCl is in equilibrium with solid AgCl. Will the solubility of AgCl be the same at 25°C, if the solvent were say $0.1\ M$ $AgNO_3$ solution? $AgNO_3$ is freely soluble in water, and it gives $0.1\ M$ Ag^+ in solution. K_{sp} is constant whether the solid dissolves in pure water or in water containing other ions. This is true even if the other ions added happen to be common to the salt under study. Let us see the effect of the added $0.1\ M$ $AgNO_3$ on the solubility equilibrium.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
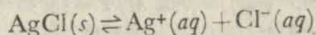
According to Le Chatelier's principle, external addition of $Ag^+(aq)$ (from $AgNO_3$) will shift the equilibrium from right to left. One expects the solubility to decrease and more AgCl to precipitate out of solution. The disturbance of the equilibrium here occurs only by the silver ions provided by silver nitrate. The nitrate ion has no effect since it is not a constituent in the equilibrium process. A decrease in the solubility of a salt occurs upon the addition of an ion that is common to the salt. How much is the decrease in solubility?

Example 11.4 (a) What is the solubility of AgCl in $0.1\ M$ $AgNO_3$ solution? (b) What is the solubility of AgCl in a $0.1\ M$ NaCl solution?

(a) Let the solubility of AgCl be x mol litre^{-1}. This provides x mol litre^{-1} each of Ag^+ and Cl^-. In addition, the solution already contains $0.1\ M$ each of Ag^+ and NO_3^-.

Amount of Cl^- in solution $= x$
Amount of Ag^+ in solution $= x + 0.1$
$$K_{sp}\ (AgCl) = 1.8 \times 10^{-10} = [Cl^-]\ [Ag^+]$$
$$= x(x + 0.1)$$
$$= x^2 + 0.1\ x$$

Since the value of K_{sp} is small, we expect the value of x also to be small, especially compared to $0.1 M$. We can then neglect x^2 and write, as a reasonable approximation:

$$K_{sp} = 1.8 \times 10^{-10} \approx x(0.1)$$
$$\text{hence,} \quad x = 1.8 \times 10^{-9}\ \text{mol litre}^{-1}$$

This is the solubility of AgCl in $0.1\ M$ $AgNO_3$.

(b) Let the solubility be y mol litre^{-1}, providing y mol litre^{-1} each of Ag^+ and Cl^-. The solution already contains 0.1 mol litre^{-1} each of Na^+ and Cl^-. As in (a), we can write

$$K_{sp}\ (AgCl) = 1.8 \times 10^{-10} = (y + 0.1)\ y = 0.1\ y$$

or the solubility of AgCl in $0.1\ M$ NaCl solution, y, is 1.8×10^{-9} mol litre^{-1}.

Notice in the example above that NO_3^- (in a) and Na^+ (in b) have no effect on the solubility. But Ag^+ and Cl^- which are ions common to AgCl affect the solubility by altering the equilibrium. This is termed the *common ion effect*.

11.4 APPLICATIONS OF SOLUBILITY PRODUCT AND THE COMMON ION EFFECT

Solubility product offers a means of determining whether precipitation occurs from a given solution or not. In a system AB, if the product of the concentrations of the ions A^+ and B^-, termed the *ion product*, is larger than the solubility product, the solution is ' supersaturated ' and precipitation occurs. If the ion product is less than the solubility product, the solution of AB is unsaturated and no precipitation occurs. This concept of the solubility product finds a number of applications.

Example 11.5 Will calcium sulphate precipitate when: (a) equal volumes of 0·02 M $CaCl_2$ and 0·0004 M Na_2SO_4 are mixed and (b) equal volumes of 0·08 M $CaCl_2$ and 0·02 M Na_2SO_4 are mixed? $[K_{sp}(Ca\,SO_4) = 2\cdot4 \times 10^{-5}]$

We need the concentration of each ion after mixing. When equal volumes of two solutions are mixed, the concentration of each species in solution becomes half of what it was before mixing.

(a) $\qquad\qquad\qquad [Ca^{2+}\,(aq)] = (0\cdot02\ M)/2 = 1 \times 10^{-2}\ M$
$\qquad\qquad\qquad [SO^{2-}_4(aq)] = (0\cdot02\ M)/2 = 1 \times 10^{-2}\ M$

The ion product $[Ca^{2+}\,(aq)]\,[SO^{2-}_4\,(aq)] = 2 \times 10^{-6}\ M$

The solubility product $[Ca^{2+}\,(aq)]_{eq}\,[SO^{2-}_4(aq)]_{eq} = 2\cdot4 \times 10^{-5}$ where the subscript ' eq ' emphasises that K_{sp} is the ion product under solubility equilibrium condition. Since the product is less than K_{sp}, $CaSO_4$ will not precipitate.

(b) $\qquad\qquad\qquad [Ca^{2+}\,(aq)] = (0\cdot08M)/2 = 4 \times 10^{-2}\ M$
$\qquad\qquad\qquad [SO^{2-}_4\,(aq)] = (0\cdot02\ M)/2 = 2 \times 10^{-2}\ M$

The ion product $[Ca^{2+}(aq)]\,[SO^{2-}_4\,(aq)] = 4 \times 10^{-4}\ M$ which is greater than K_{sp}. Therefore, $CaSO_4$ will precipitate.

Solubility product and the common ion effect are utilised in the qualitative analysis of inorganic ions. Table 11.3 lists the values or K_{sp} of some inorganic sulphides in water. The sulphides listed in the right-hand column of Table 11.3 have larger K_{sp} values (i.e. are more soluble than those in the left-hand column). In qualitative analysis, detection of these metal ions is achieved by passing hydrogen sulphide gas through their aqueous solutions. Precipitation of the metal sulphides occurs when the ion product $[M^{2+}(aq)]\,[S^{2-}(aq)]$ exceeds the K_{sp}.

If an aqueous solution of the metal ions is acidified before H_2S is passed, ionisation of H_2S to H^+ and S^{2-} will be suppressed due to the presence of

Table 11.3 Solubility Product values of Inorganic Sulphides in Water (18°C)

Sulphide	K_{sp}	Sulphide	K_{sp}
PbS	$3\cdot4 \times 10^{-28}$	MnS	$1\cdot4 \times 10^{-16}$
CdS	$3\cdot6 \times 10^{-29}$	ZnS	$1\cdot2 \times 10^{-23}$
CuS	$8\cdot5 \times 10^{-45}$	NiS	$1\cdot4 \times 10^{-24}$
HgS	$41\cdot0 \times 10^{-53}$	CoS	$3\cdot0 \times 10^{-26}$

hydrogen ions from the acid (common ion effect). The amount of S^{2-} in a solution is reduced and the ion product of MnS, ZnS, NiS and CoS will not exceed the corresponding K_{sp}. So, these sulphides remain in solution, while PbS, CdS, CuS and HgS precipitate. The latter four sulphides are usually referred to as group II sulphides in qualitative analysis. Thus, in an aqueous solution containing, Pb^{2+} and Mn^{2+} ions, we can separate Pb^{2+} by first acidifying the solution and then adding H_2S; Pb^{2+} will precipitate as PbS while Mn^{2+} remains in solution. In order to precipitate metal sulphides like MnS, ZnS, NiS, and CoS (termed group IV sulphides in qualitative analysis), one adds a few ml of ammonium hydroxide to solutions containing these metal ions. The OH^- of NH_4OH reacts with the H^+ of H_2S, depleting the latter. This causes an increase in the amount of H_2S ionising and consequently the concentration of sulphide ions increases; when the S^{2-} concentration increases beyond the required amount, the corresponding metal sulphide precipitates from solution.

The concept of solubility product finds use in chemical industry. Sodium carbonate is manufactured by the Solvay process by decomposing sodium bicarbonate ($NaHCO_3$). In the Solvay method, carbon dioxide gas is bubbled through a solution of ammoniacal brine (i.e. NH_4OH and NaCl in water) where it reacts to produce $NaHCO_3$ and NH_4HCO_3. Out of the four species present in solution, NH_4Cl, NaCl, $NaHCO_3$ and NH_4HCO_3, the solubility product of $NaHCO_3$ is the lowest and is easily exceeded. $NaHCO_3$ separates out and is isolated and decomposed to produce Na_2CO_3 in large quantities.

Isolation of magnesium chloride from sea water has also been achieved using the principles of solubility product and common ion effect. From a mixture containing sodium and magnesium chlorides, sodium chloride can be precipitated out when we pass HCl gas through an aqueous solution of the mixture. The ion product for NaCl exceeds its solubility product upon the addition of Cl^- from HCl, and NaCl precipitates. The solubility product of $MgCl_2$ is not exceeded, however, and it remains in solution and can be filtered.

11.5 ACIDS AND BASES

We have been discussing solutions of salts and their equilibria. But how are salts formed? This question was recognised as early as three hundred years ago and Robert Boyle (who gave us the famous gas law that goes by his name) suggested that salts are formed by the reaction of an acid with an alkali (a base). According to Boyle, an acid was a compound that possessed many characteristic properties such as (*i*) a sour taste (hence the name from the Latin word *acidus*, meaning sourness), (*ii*) changes the colour of certain plant dyes (called litmus) to red, (*iii*) liberates gaseous hydrogen from metals, and (*iv*) gets spent or neutralised by an alkali. Some examples of acids are muriatic acid (HCl!) and oil of vitriol (H_2SO_4!). Similarly, an alkali was defined as a compound which (*i*) changes the colour of litmus to blue, (*ii*) reacts with acids to give salts, and (*iii*) has a bitter taste, and so on. Examples of some alkalies are caustic soda (NaOH), baryta water $Ba(OH)_2$, lime water $Ca(OH)_2$, and caustic potash (KOH).

As ideas on acids and bases developed, the French chemist Lavoisier postulated that all acids contain oxygen. Soon, this was shown to be not always true (e.g. HCl, HCN). Arrhenius suggested that an acid is a substance that produces hydrogen ions in water and that a base is one that produces hydroxide ions

in water. This is a theory that assumes a simple dissociation of these subs-
tances as

$$HCl \rightleftharpoons H^+ + Cl^- \qquad \text{(ACID)}$$
$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$
$$KOH \rightleftharpoons K^+ + OH^- \qquad \text{(BASE)}$$
$$NH_4OH \rightleftharpoons NH^+_4 + OH^-$$
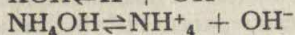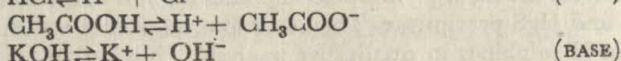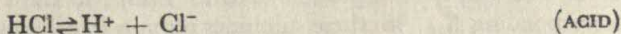
While the Arrhenius concept of acids and bases is useful in many cases, it
suffers from many inadequacies. Even ammonia behaves as a base and so does
pyridine, even though they do not contain OH^-. Many pure acids are covalent
in nature, so something more than mere dissociation into hydrogen ions must
be involved when they are dissolved in water.

11.5.1 Brönsted Theory

A useful modification of the Arrhenius idea came from Brönsted and Lowry.
They defined an acid as a substance that yields a hydrogen ion (commonly
called proton) and a base as that which accepts a proton. Thus, an acid-base
reaction involves donation of a proton by the acid to the base. A covalent
compound like HCl behaves as an acid in water because of the reaction:

$$HCl + H_2\dot{O} \rightleftharpoons H_3O^+ + Cl^-$$
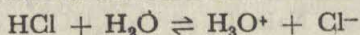
HCl reacts with water to donate a proton to the latter. Thus HCl is the *acid*
and H_2O is the *base*. We have deliberately written the above equation as a
reversible reaction. In reality, the reverse process occurs to a negligible extent;
in the reverse reaction H_3O^+ is the acid and Cl^- is the base. We have defined
here not only an acid and a base, but also introduced the idea of *conjugate
acids and bases*. It is convenient to look at the pair HCl and Cl^-. HCl is the acid
and Cl^- is the conjugate base of HCl. Likewise, water is the base while H_3O^+
is its conjugate acid. Let us look at some more examples.

$$H_2SO_4 \quad + \quad H_2O \rightleftharpoons HSO^-_4 \quad + H_3O^+ \qquad (11.1)$$
$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \qquad (11.2)$$
$$HCl \qquad + \quad NH_3 \rightleftharpoons NH^+_4 \quad + Cl^- \qquad (11.3)$$
$$H_2O \qquad + \quad H_2O \rightleftharpoons OH^- \quad + H_3O^+ \qquad (11.4)$$
$$H_2O \qquad + \quad NH_3 \rightleftharpoons NH^+_4 \quad + OH^- \qquad (11.5)$$
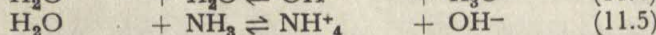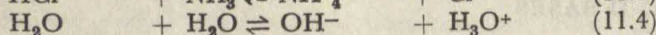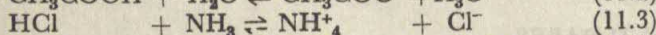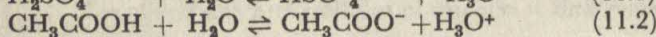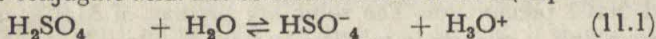
In equations (11.1) and (11.2), water acts as a base with H_3O^+ as its conjugate
base. H_2SO_4 and CH_3COOH are acids with HSO^-_4 and CH_3COO^- as their
conjugate bases respectively. In equation (11.3), HCl and Cl^- form an acid—
conjugate base pair, and NH_3 and NH^+_4 form a base-conjugate acid pair.
Equation (11.4) is interesting in that one molecule of water acts as an acid
(its conjugate base being the hydroxide ion) and the other water molecule acts
as a base (with the hydronium ion, H_3O^+, as its conjugate acid). In equation
(11.5), water acts as an acid (with hydroxide ion as its conjugate base) and
ammonia is the base with the ammonium ion as its conjugate acid.

A few points of interest arise from the Brönsted formalism: (*i*) The same
compound may act as an acid in one situation and as a base in another. (*ii*) Any
compound that acts as an acid has its conjugate base and vice versa. When
water acts as an acid, hydroxide ion is its conjugate base, and while it behaves
as a base, the hydronium ion H_3O^+ becomes its conjugate acid. (*iii*) All acid-
base reactions may be viewed as reversible reactions with a corresponding
equilibrium constant. This is why we have shown two arrows indicating equili-
brium conditions in all the above equations. In equation (11.1), the forward

reaction occurs to a much greater extent than the reverse reaction. We may say that sulphuric acid is a strong acid since it pushes the forward reaction. In other words, the tendency of sulphuric acid to donate protons to water is overwhelming. In contrast, the bisulphate anion is a weak base; it does not accept protons from the hydronium ion to any appreciable extent to push the backward reaction. In general, one finds that a strong acid has a weak conjugate base. Conversely, as equation (11.2) exemplifies, a weak acid such as acetic acid possesses a strong conjugate base as the acetate ion. The acetate ion has a greater tendency to accept a proton from H_3O^+, than acetic acid has to donate a proton to water. (*iv*) The Brönsted theory not only covers all the cases of Arrhenius but also includes many neutral molecules and ions in its classification of acids and bases (*v*) In the Brönsted definition of acids and bases, there is no special emphasis laid on any particular solvent.

We may summarise the Brönsted theory in a capsule form as follows:

$$ACID_1 + BASE_2 \rightleftharpoons CONJUGATE\ BASE_1 + CONJUGATE\ ACID_2$$
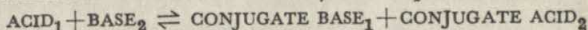
The Brönsted theory of acid-base pairs has found applications in diverse areas such as neutralisation reactions, hydrolysis behaviour, and strengths of acids and bases. This theory emphasises the role of the proton in acid-base reactions, and for this reason it is also referred to as the proton theory. Another interesting point about this theory is that it treats the proton in aqueous solution as the hydronium ion, H_3O^+ and not as an isolated entity. We might view this as a hydrated proton, or $H^+(aq)$. Recent evidence points to the basic correctness of the nature of the proton in water. While the hydration number of a proton in water may be 1, 2, 3 or 4, it is convenient to denote a hydrogen ion as H_3O^+. But let us keep in mind that it may actually be H_3O^+, $H_5O^+_2$, or $H_9O^+_4$, i.e. $H^+(H_2O)_n$. While we shall have occasion to discuss some failings of the Brönsted formalism a little later, let us now look at how this has helped in understanding some phenomena.

11.5.2 Hydrolysis
In an acid-base reaction involving water, water acts both as a base and as an acid, depending on the conditions involved:

$$HA + H_2O \rightarrow H_3O^+ + A^-$$
$$B + H_2O \rightarrow HB^+ + OH^-$$
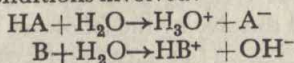
Another example of this dual behaviour of water was also shown in equation (11.5). Such reactions where decomposition of water molecules occurs are termed *hydrolysis* reactions (*hydro*=water, *lysis*=break). This phenomenon is rather widespread in chemistry and it is worthwhile looking at some of these cases.

When a salt like sodium chloride is dissolved in water, the only thing that happens is the hydration of ions. No chemical reaction occurs. The salt does not behave either as a Brönsted acid or a Brönsted base towards water. This may be represented as:

$$NaOH\ (aq) \rightarrow Na^+(aq)\ + OH^-(aq)$$
$$HCl\ (aq)\ \rightarrow H_3O^+(aq)\ + Cl^-(aq)$$

$$NaOH(aq) + HCl(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_3O^+(aq) + OH^-(aq)$$
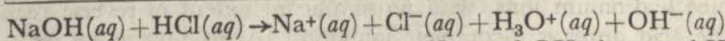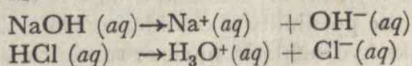
Since NaOH in aqueous solution exists as Na^+ and OH^- ions, and HCl as H^+ and Cl^- ions (with all ions aquated or hydrated), the net reaction is,

$$OH^-(aq) + H_3O^+ \rightarrow 2H_2O$$
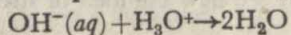
In other words, Na^+ and Cl^- do not participate in any neutralisation (acid-base) reaction. They remain simply hydrated. Salts of strong acids and strong bases have no reaction towards water.

When we turn to a salt made from a strong acid and weak base, like ammonium chloride, or from a strong base and weak acid such as sodium acetate, the situation changes. In the case of NH_4Cl, the reactions are:

$$NH_4Cl \rightarrow NH^+_4 + Cl^-$$
$$NH^+_4 + H_2O \rightarrow NH_3 + H_3O^+$$
$$Cl^- + H_2O \rightarrow Cl^- (aq)$$
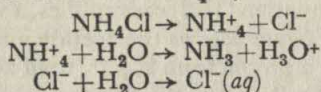
HCl is a strong acid and its conjugate base Cl^- does not react with water; NH_3 is weak but its conjugate acid NH_4^+ is a strong acid that reacts with water (as base). Hence when ammonium chloride is dissolved in water, the chloride ion is passive but the ammonium ion generates H_3O^+ ions, making the solution of the salt acidic.

Let us examine the case of a salt like sodium acetate. In water, this ionises completely to Na^+ and CH_3COO^- ions. We know that sodium ion does not react with water, but the acetate ion is a strong conjugate base of the weak acid, acetic acid:

$$Na^+ + H_2O \rightarrow Na^+ (aq)$$
$$CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$$
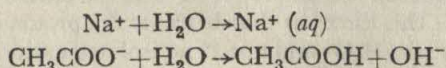
The net effect of dissolving sodium acetate in water is to break up the water molecules (hydrolysis) to produce acetic acid and hydroxide ion (which is a strong base). As a result the solution will be mildly alkaline.

There are yet other ions which can react both with hydronium and with hydroxide ions. Such a dual property is called *amphoterism*. For example, if we take aluminium ion in water:

$$[Al(H_2O)_6]^{3+} + OH^- \rightarrow [Al(OH)(H_2O)_5]^{2+} + H_2O$$
$$[Al(OH)(H_2O)_5]^{2+} + OH^- \rightarrow [Al(OH)_2(H_2O)_4]^+ + H_2O$$
$$[Al(OH)_2(H_2O)_4]^+ + OH^- \rightarrow [Al(OH)_3(H_2O)_3] + H_2O$$
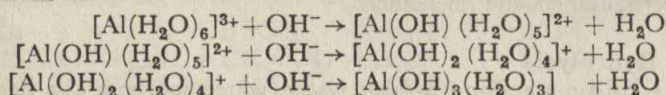
The neutral species $[Al(OH)_3(H_2O)_3]$ comes out of solution. This species can react in acid medium and dissolve by the following reaction:

$$[Al(OH)_3(H_2O)_3] + H_3O^+ \rightarrow [Al(OH)_2(H_2O)_4]^+ + H_2O$$
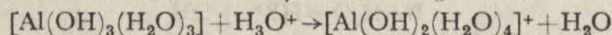
It can also react with a base:

$$[Al(OH)_3(H_2O)_3] + OH^- \rightarrow [Al(OH)_4(H_2O)_2]^-$$
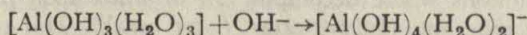
We call substances that react both with acids and bases as *amphoteric*.

11.5.3 Strengths of Acids and Bases

The Arrhenius concept of acids and bases mentions that these compounds dissociate to produce H^+ and OH^- ions respectively. The Brönsted theory modifies this somewhat to say that an acid and a base react to produce conjugate partners. This offers the possibility of considering the reaction as an ionisation equilibrium. Acids like hydrochloric, nitric or sulphuric acid, ionise completely to produce hydronium ions, with no significant extent of reverse reactions. But acetic acid displays incomplete ionisation. Acids that ionise to a large extent to produce H_3O^+ are termed ' strong ' and acids that ionise weakly are termed ' weak ' acids. Let us see how the idea of strength of an acid can be formulated quantitatively.

The ionisation of an acid HA in water is represented by,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
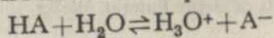
The equilibrium constant for this process is given by,

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \quad \text{or,} \quad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

We have omitted the concentration of water in the second equation since being large, it is essentially unchanged. The equilibrium constant K_a is defined as the ionisation constant. The subscript 'a' denotes that it is for acid ionisation. The quantity K_a measures the 'strength' of an acid. An acid that has a K_a value greater than ten is generally considered a strong acid. Examples of strong acids are the mineral acids (HCl, H_2SO_4, HNO_3, $HClO_4$, etc.). Acids with ionisation constants less than unity, are regarded as weak. Examples of weak acids are phenol and inorganic acids like HCN, H_2S, etc. Table 11.4 lists the ionisation constants of some acids.

Table 11.4 Ionisation Constants for Some Acids in Water at 25°C

Acid	K_a	Acid	K_a
HCl	∞	CH_3COOH	$1\cdot75 \times 10^{-5}$
HNO_3	∞	C_6H_5COOH	$6\cdot17 \times 10^{-5}$
HF	$7\cdot25 \times 10^{-4}$	C_6H_5OH	$1\cdot0 \times 10^{-10}$
HCOOH	$1\cdot78 \times 10^{-4}$	Toluene	$1\cdot0 \times 10^{-37}$

Acids containing more than one ionisable hydrogen are called *polyprotic* acids. For example, sulphuric acid can ionise to give two H_3O^+ ions in two successive stages. Hence it is a diprotic acid.

$$H_2SO_4 + H_2O \overset{K_{a1}}{\rightleftharpoons} HSO_4^- + H_3O^+$$

$$HSO_4^- + H_2O \overset{K_{a2}}{\rightleftharpoons} SO_4^{2-} + H_3O^+$$
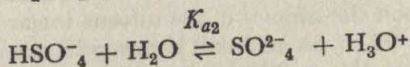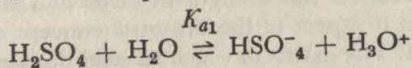
The corresponding dissociation equilibria are written as

$$K_{a1} = \frac{[H_3O^+][HSO_4^-]}{[H_2SO_4]} \quad \text{and} \quad K_{a2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}$$

It is found that the value K_{a1} is enormously high, but K_{a2} has a value of $1\cdot3 \times 10^{-2}$. This means that in aqueous solution, sulphuric acid completely ionises to produce H_3O^+ and HSO_4^-, while the HSO_4^- ionises much less to yield H_3O^+ and SO_4^{2-} ions. In a solution of sulphuric acid, both equilibria exist simultaneously, and both constants must be satisfied by the concentrations of all the species present.

The ionisation equilibria of bases are treated similarly.

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$
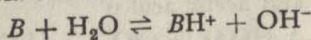
$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Here again, a large value of K_b (subscript 'b' referring to base) denotes a strong base. Table 11.5 lists the ionisation constants of some bases.

Table 11.5 Ionisation Constants of Some Bases in Water at 25°C.

Base	K_b	Base	K_b
NaOH	∞	Benzylamine	2.2×10^{-5}
Ca(OH)$_2$	3.7×10^{-3}	Aniline	4.0×10^{-10}
NH$_4$OH	1.8×10^{-5}		

Example 11.6 Calculate the degree of ionisation of a 0·4 M acetic acid solution in water.

Let us abbreviate acetic acid as HOAc. The equilibrium is,

$$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$$
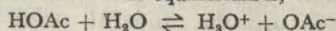
From Table 11.4, $K_a = 1.8 \times 10^{-5}$. Then,

$$1.8 \times 10^{-5} = \frac{[H_3O^+] \ [OAc^-]}{[HOAc]}$$

The degree of ionisation a is defined as the fractional molarity of the ionised species. In this equilibrium $0.4 \ (1-a)M$ of HOAc, $0.4aM$ of H_3O^+ and 0.4_aM of OAc$^-$ are present. Since K_a value is small (10^{-5}), a is expected to be small compared to unity. Hence we write approximately:

$$1.8 \times 10^{-5} = (0.4 \ a)^2/0.4 \ \text{or} \ a = 6.71 \times 10^{-3}$$

The amount of H_3O^+ (and OAc$^-$) present in 0·4 M acetic acid is 0·4 a, and is, therefore, 2.68×10^{-3} mol litre^{-1}. This amounts to 0·67 per cent of acetic acid ionising to yield acetate and hydronium ions.

NOTE: If the degree of ionisation is appreciable, say 10 per cent then we cannot omit a in comparison to the concentration of undissociated species. That is, we cannot write 0·4 $(1-a) = 0.4$. In these cases, the quadratic equation should be solved to obtain the value of a.

We have so far discussed the strength of acids and bases only in aqueous solutions. An important aspect of the Brönsted concept of acids and bases is the role of the solvent. The extent to which an acid donates the proton (i.e. the strength) depends upon the affinity of the solvent towards the proton, or the *basicity* of the solvent. Thus, an acid that is strong in one solvent may be quite weak in another. According to Brönsted, when an acid is dissolved in water, it ionises to its conjugate base and produces the acid H_3O^+. This is true of all acids towards which water acts as a base. The conjugate acid produced by all acids stronger than water is the hydronium ion. Therefore, in aqueous solution, all acids stronger than water appear equally strong. In other words, water is a strong enough base to ' level out ' or obscure differences between acid strengths. This is referred to as the *levelling effect*. The differences in the strengths of acids such as hydrochloric, nitric or sulphuric acids cannot be distinguished in water.[*] In order to differentiate the strengths of these strong acids, one must choose a solvent that is less basic (or more acidic) than water, so that it accepts protons more reluctantly than does water. One such solvent is acetic acid. The reaction between perchloric acid and acetic acid is

$$HClO_4 + HOAc \rightarrow ClO^-_4 + H_2OAc^+$$
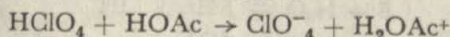
In acetic acid as solvent, the strengths of some inorganic acids vary as, $HClO_4 > H_2SO_4 > HCl > HNO_3$.

[*]This is analogous to weighing objects heavier than 100 g on a balance of 100 g capacity. Such a balance cannot distinguish between two masses of 110 g and 200 g.

11.5.4 Ionisation of Water

As shown in section 11.5.1, the acid-base equilibrium between two water molecules can be written as

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
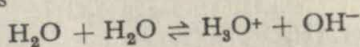
Overall the solution is electrically neutral. Yet even the purest sample of water conducts electricity to a small extent indicating the presence of ions. The dissociation equilibrium of water (in water) is,

$$K = \frac{[H_3O^+]\,[OH^-]}{[H_2O]^2}$$

Since the solvent medium is water, the denominator is a constant and we may write a modified equilibrium constant as

$$K_w = [H_3O^+]\,[OH^-]$$

The constant K_w is called the *ionic product of water*. Since it is an equilibrium constant, it must depend on temperature (see Table 11.6). At 25°C, K_w has a value 1.0×10^{-14}. Since upon ionisation the amount of H_3O^+ is the same as that of OH^-, we get a value of 10^{-7} M as the concentration of H_3O^+ (and of OH^-) ions in water at this temperature.

In pure water, all the H_3O^+ and OH^- ions arise only from the ionisation of water molecules. The concentration of each of these at 25°C is 10^{-7} M. These concentrations are related to each other by K_w. In neutral solutions, i.e. in aqueous solutions of substances that do not behave as acids or bases towards water, this concentration of H_3O^+ or OH^- does not change. For example when sodium chloride is dissolved in water neither Na^+ nor Cl^- ion behaves as an acid or base towards water. Hence in this solution, the concentrations of H_3O^+ and OH^- are the same (10^{-7} M) as in pure water. In an aqueous solution of say ammonia, the auto-ionisation of water yields 10^{-7} M of hydroxide ion. Besides this, ammonia behaves as a base towards water and produces more OH^- ions (see section 11.5.1). The concentration of OH^- ions becomes greater than $10^{-7}M$. In aqueous ammonia solutions, $[OH^-] > [H_3O^+]$. In a similar fashion, when sulphuric acid is dissolved in water, $[H_3O^+] > [OH^-]$. We, therefore, define an aqueous solution as neutral if $[OH^-] = [H_3O^+]$, as acidic if $[H_3O^+] > [OH^-]$ and as basic if $[OH^-] > [H_3O^+]$.

Table 11.6 Ionic Product of Water at Several Temperatures

Temp, °C	K_w	Temp. °C	K_w
0	1.14×10^{-15}	40	2.71×10^{-14}
10	2.95×10^{-15}	50	5.30×10^{-14}
25	1.00×10^{-14}		

11.5.5 The pH Scale

The concentrations of H_3O^+ and OH^- in most solutions we ordinarily deal with are in the range 10^{-1} to 10^{-7} M. A convenient way of expressing such small concentrations was suggested by Sorensen who introduced the *p*H notation (after the French expression *puissance de hydrogen*, meaning the strength or

the concentration of hydrogen). pH is defined as the negative logarithm (to the base 10) of the concentration of hydrogen ions $[H_3O^+]$ in solution.

$$pH = -\log_{10}[H_3O^+]$$
$$\text{or, } [H_3O^+] = (10)^{-pH}$$

In pure water, $[H_3O^+]=1.0 \times 10^{-7}$ M. Therefore, $pH=7$. In a solution of 0.001 M hydrochloric acid in water, the concentration of hydrogen ions is also 0.001 M or the pH is 3.0.

Similar to the above expression for pH, we may also define other terms:

$$pOH = -\log[OH^-]$$
$$pK_w = -\log K_w$$
$$pK_a = -\log K_a$$
$$pK_b = -\log K_b$$
$$p(OAc) = -\log[\text{acetate}^-]$$

Example 11.7 (a) Express the pH, pOH, and pK_w of water at 25°C. (b) What is the pH of a solution of 0.0001 M sodium hydroxide in water?

a) We know that for water at 25°C,

$$K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$$
$$\text{and } [H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$$
$$\text{hence } pH = -\log[H_3O^+] = 7.0$$
$$pOH = -\log[OH^-] = 7.0, \text{ and}$$
$$pK_w = -\log K_w = 14.0$$

(b)
$$NaOH + H_2O \rightarrow Na^+ (aq) + OH^- (aq)$$

Complete dissociation occurs and one mole of NaOH yields one mole of OH^-. Hence $[OH^-]=0.0001$ $M=10^{-4}$ M and $pOH=-\log[OH^-]=4.0$. Sodium hydroxide being a base produces no H_3O^+ in water. But the OH^- produced by NaOH disturbs the equilibrium

$$H_3O^+ + OH^- \rightleftharpoons H_2O + H_2O$$
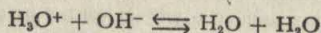
and shifts it to the right. The ionic product of water is 10^{-14} and is a constant. Hence, to maintain K_w constant, the amount of H_3O^+ decreases from the value (10^{-7} M) in pure water. The relation between H_3O^+ and OH^- is

$$[H_3O^+][OH^-] = K_w$$
$$\text{or } pH + pOH = pK_w = 14.0$$

we find that $pOH=4.0$. Hence $pH=14.0-4.0=10.0$.

Notice from the above example that the pH of pure water, and of a neutral aqueous solution is 7.0. So is the pOH. If the solution is acidic, pH becomes less than 7. Simultaneously the pOH becomes greater than 7. In a basic solution, $pH>7$ and $pOH<7$.

Table 11.7 pH of Some Substances

Substance	pH	Substance	pH
Bar soap solution	8.5	Distilled water	7.0
Human blood	7.3	Vinegar solution	4.0

pH is a quantitative measure of the acidity of a solution. Table 11.7 gives a list of some common substances and their acidities in terms of pH.

Example 11.8 What is the pH of a 0.01 M solution of $Ca(OH)_2$ in water?

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$
$$0.01\ M \qquad 0.01\ M\ 0.02\ M$$
$$p\text{OH} = -\log\ (2 \times 10^{-2}) = -(0.301-2) = 1.7$$
$$p\text{H} = p\text{K}_w - p\text{OH} = 14.0 - 1.7 = 12.3$$

Example 11.9 What is the pH of 0.4 M acetic acid solution in water?

We have calculated H_2O^+ as 2.68×10^{-3} mol litre^{-1} in Example 11.6 for this solution. Hence $p\text{H} = -\log\ (2.68 \times 10^{-3}) = -(0.428-3.0) = 2.57$.

Both the examples shown above exemplify the point that acidic solutions always have a pH less than 7 while in a basic solution the pH is always greater than 7. This is so because an acid contributes some amount of H_3O^+ to the solution, besides the 10^{-7} M of H_3O^+ arising out of water. The total H_3O^+ concentration in an acidic solution is always greater than 1×10^{-7} M, thereby making the pH less than 7. The following example is especially interesting since it clarifies what apparently seems to be a paradox.

Example 11.10 Calculate the pH of a 1.0×10^{-8} M solution of HCl.

If we solve this problem by the method given in the preceding examples we obtain,
$$p\text{H} = -\log\ [H_3O^+] = -\log\ 1 \times 10^{-8} = 8$$

This is obviously wrong because $p\text{H} = 8$ corresponds to a basic solution and the pH of water to which some acid has been added has to be less than 7. The error lies in the fact that in all preceding examples we have ignored the concentration of protons coming from the ionisation of water. This assumption is quite valid when the concentration of protons arising from the ionisation of the acid is very large compared with that from water. However, in the case of very dilute acidic solution when the H$^+$ concentrations from the acid and the water are comparable, one must also consider the equilibrium

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$K_w = [H_3O^+]\ [OH^-] = 1.0 \times 10^{-14}$$
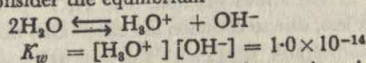
where $[H_3O^+]$ represents the total concentration of hydrogen ions in solution which is equal to the sum of contribution of hydrogen ion concentration from water, $[H_3O^+]_{H_2O}$ and from HCl, $[H_3O^+]_{HCl}$.

$$[H_3O^+] = [H_3O^+]_{H_2O} + [H_3O^+]_{HCl}$$

The proton concentration from water ionisation is equal to the hydroxyl ion concentration from the same source. Therefore,

$$[H_3O^+]_{H_2O} = [OH^-]_{H_2O} = X$$
and $$[H_3O^+]_{total} = X + [H_3O^+]_{HCl}$$

Since HCl is a strong acid, it is completely ionised. Thus,

$$[H_3O^+]_{HCl} = 1.0 \times 10^{-8}$$
and $$[H_3O^+]_{total} = X + 1.0 \times 10^{-8}$$

Substituting the values of $[H_3O^+]_{total}$ and $[OH^-]$ in the equilibrium expression, we obtain,

$$(X+10^{-8})\ (X) = 1.0 \times 10^{-14}$$
or, $$X^2 + 10^{-8}\ X - 10^{-14} = 0$$
or, $$X = -10.5 \times 10^{-8} \text{ and } X = 9.5 \times 10^{-8}$$

As concentration cannot be negative, the negative solution is rejected. Therefore, $X = 9.5 \times 10^{-8}$ and

$$[H_3O^+]_{total} = X + 10^{-8} = 9.5 \times 10^{-8} + 10^{-8}$$
$$= 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$$

The pH of the solution can be computed as follows:
$$p\text{H} = -\log\ [H_3O^+] = -\log\ 1.05 \times 10^{-7} = 6.98$$

Thus we find that the hydrogen ion concentration in the solution $(1 \cdot 05 \times 10^{-7})$ is more than that produced by HCl alone (10^{-8}). By taking into consideration the ionisation of the water, it can be shown that no matter how dilute the solution, the pH of an acid solution is always less than 7. By the same consideration no matter how dilute the solution, the pH of a base is always more than 7.

Also note that

$$[OH^-]_{H_2O} = [H_3O^+]_{H_2O} = 9 \cdot 5 \times 10^{-8}$$

The degree of ionisation of water is decreased by the presence of strong acid (common ion effect). If HCl were absent, the concentration of H_3O^+ from water would be 1×10^{-7} instead of $9 \cdot 5 \times 10^{-8}$ M.

The common ion effect that was responsible in suppressing the ionisation of water, thereby reducing the pH to less than 7, also operates in another important situation. Look at example 11.11.

Example 11.11 (*a*) What is the pH of $0 \cdot 1$ M acetic acid? (*b*) What will be the pH after adding $0 \cdot 05$ moles of HCl to a litre of solution (*a*)? (*c*) What is the pH of a solution containing $0 \cdot 1$ M acetic and $0 \cdot 1$ M sodium acetate? (*d*) What will be the change in pH if we add $0 \cdot 05$ moles of HCl to a litre of the solution (*c*)?

(*a*) K_a of acetic acid $= 1 \cdot 8 \times 10^{-5}$

$$H_2O + CH_3COOH \rightleftharpoons CH_3COO + H_3O^+$$
$$0 \cdot 1 \ M - x \qquad\qquad x \qquad\qquad x$$
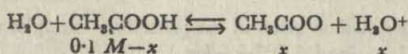
$$1 \cdot 8 \times 10^{-5} = \frac{x^2}{0 \cdot 1 - x} = \frac{x^2}{0 \cdot 1} \quad \text{since } x \ll 0 \cdot 1$$

hence
$$x = 1 \cdot 34 \times 10^{-3} = [H_3O^+]$$
and
$$p\text{H} = -(-3 \cdot 00 + 0 \cdot 1271) = 2 \cdot 87$$

(*b*) Addition of $0 \cdot 05$ moles of HCl amounts to addition of 5×10^{-2} moles of H_3O^+ per litre, since HCl ionises completely. This addition of H_3O^+ will drive the ionisation equilibrium of acetic acid towards left in the above reaction. The H_3O^+ provided by acetic acid will not be the same as in (*a*), but less, due to common ion effect. Call this x. Now:

$$[H_3O^+] = x + 0 \cdot 05, \ [CH_3COO^-] = x, \ [CH_3COOH] = 0 \cdot 1 - x$$

and
$$K_a = 1 \cdot 8 \times 10^{-5} = \frac{x(x + 0 \cdot 05)}{(0 \cdot 1 - x)} = \frac{x(0 \cdot 05)}{0 \cdot 1}$$

hence $x = 3 \cdot 6 \times 10^{-5}$ M, i.e. ionisation of acetic acid is suppressed by HCl addition.

$$[H_3O^+] = x + 0 \cdot 05 \approx 0 \cdot 05 \text{ since } x \ll 0 \cdot 05$$

hence
$$p\text{H} = -\log (5 \times 10^{-2})$$
$$= -(-2 + 0 \cdot 6990) = 1 \cdot 3$$

The change in the pH in (*b*) from (*a*) is almost entirely due to the added acid.

(*c*) $0 \cdot 1$ M sodium acetate yields $0 \cdot 1$ M acetate ion; the salt ionises completely. The added acetate ion must, by the common ion effect, reduce the ionisation of acetic acid. This is similar to the case in (*b*). The concentration of H_3O^+ will not be what was calculated in (*a*), i.e. in the absence of the salt, but will be some amount denoted here as x. The amount of acetate is then $x + 0 \cdot 1$.

$$K_a = 1 \cdot 8 \times 10^{-5} = \frac{x(x + 0 \cdot 1)}{(0 \cdot 1 - x)} = \frac{x(0 \cdot 1)}{(0 \cdot 1)}$$
$$= x = [H_3O^+]$$
hence $p\text{H} = -\log (1 \cdot 8 \times 10^{-5}) = 4 \cdot 74$

(*d*) In this case, $0 \cdot 05$ mol of the added HCl will combine with an equal amount of acetate anion to produce acetic acid. Hence,

$$[CH_3COOH] = 0 \cdot 1 + 0 \cdot 05 = 0 \cdot 15 \ M, \text{ and}$$
$$[CH_3COO^-] = 0 \cdot 1 - 0 \cdot 05 = 0 \cdot 05 \ M$$

$$K_a = 1.8 \times 10^{-5} = \frac{H_3O^+(0.05)}{(0.15)} = \frac{[H_3O^+]}{3}$$

$$[H_3O^+] = 5.4 \times 10^{-5} \text{ and } pH = -\log (5.4 \times 10^{-5}) = 4.27$$

11.5.6 Buffer Solutions

Example 11.11 illustrates an important point. Addition of either common ion, H_3O^+ or acetate, to a solution of the weak acid changes the pH considerably. Addition of HCl changed the pH of acetic acid from 2·9 to 1·3, but the addition of the same amount of HCl to an equimolar mixture of the weak acid and its salt changed the pH only slightly, from 4·7 to 4·3.

In general, we find that a solution containing a weak acid and its salt, or a weak base and its salt, has a tendency to maintain its pH relatively constant on addition of small amounts of acid or base. Solutions which thus resist an alteration in their hydrogen ion concentrations are termed *buffer* solutions.

How does a buffer solution resist a change in its pH? We saw in Example 11.11 that the added HCl reacts with the acetate ions of the buffer solution to produce acetic acid. H_3O^+ ions are removed by the acetate to produce acetic acid. The net effect is to vary the pH only slightly.

Consider another kind of buffer solution: a solution containing the weak base ammonium hydroxide and its salt ammonium chloride.

$$NH_4OH \rightleftharpoons NH^+_4 + OH^- \qquad NH_4Cl \rightarrow NH^+_4 + Cl^-$$
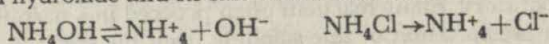
The concentration of NH^+_4 is much larger than OH^- because the salt ionises completely, but not the base. If we add a little acid to this buffer, OH^- will be removed to form water. Consequently, more base ionises to produce OH^-. Conversely, when a base is added to the buffer the ammonium ions react to form more NH_4OH.

Let us look at this in a quantitative fashion. Ionisation of a weak acid to yield protons and salt (i.e. conjugate base) is represented as

$$H_2O + HA \rightleftharpoons H_3O^+ + A^-$$
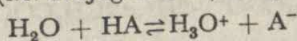
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Taking logarithms and multiplying by (-1),

$$-\log K_a = -\log[H_3O^+] - \log[A^-] + \log [HA]$$

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

$$\text{or, } pH = pK_a + \log \frac{[A^-]}{[HA]}$$

In these equations, pK_a is a constant and the variation in pH arises essentially because of a change in the molar ratio of conjugate base and acid. If the acid-salt combination were of a buffer type (weak acid and its salt), addition of either H_3O^+ or OH^- changes the ratio $[A^-]/[HA]$ only slightly, thus causing only a minor variation in the pH. The relation for a weak base is,

$$pOH = pK_b + \log \frac{[BH^+]}{[B]}$$

$$pOH = pK_b + \log \frac{[\text{CONJUGATE ACID}]}{[\text{BASE}]}$$

By the same mechanism, the pOH (and hence pH which is $14-pOH$) of a weak base-salt solution is maintained. This will also be a buffer solution.

The equations above offer a way of determining dissociation constant of a weak acid or a weak base. Thus, to determine the pH of a weak acid, we prepare a solution containing equal molar concentrations of the acid and its salt. Then $[A^-]=[HA]$, $\log [A^-]/[HA]$ vanishes, and the pH of the solution when measured gives us the pK_a of the acid. Likewise, the measured pH of an aqueous solution of an equimolar mixture of a weak base and its salt gives the pK_b of the base.*

Many reactions of biological and industrial importance occur under rather stringent pH conditions. For example, the uptake of oxygen by blood and its transport from the lungs to other parts of the body is done in the pH range of 7·3–7·5. The electrolytes present in blood act as a buffer solution to maintain the pH of blood in this desired range. Any alteration in the pH of blood would lead to pathological conditions. Similarly, the pH of the digestive fluids in the gastric juice is maintained between 1·5 and 2·0. Any alteration in the pH leads to vomiting and ulceration. Control of pH in such biological systems is crucial because the enzymes which catalyse biochemical reactions function best at optimum pH values. Deviations from these pH values hinder the efficiency of these bio-catalysts.

Even in the laboratory, many reactions often proceed in a narrow pH range. For example, the precipitation of zinc sulphide from the chloride,

$$H_2S+ZnCl_2 \rightleftharpoons ZnS+2HCl$$
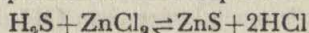
is not very efficient since the hydrogen ions formed accumulate in solution and start driving the reaction towards left. However, if we pass hydrogen sulphide gas through a solution of zinc chloride in presence of some acetate (sodium acetate), all the zinc precipitates as the sulphide.

$$H_2S+ZnCl_2 \rightarrow ZnS+2H^++2Cl^-$$
$$2CH_3COO^-+2H^+ \rightleftharpoons 2CH_3COOH$$
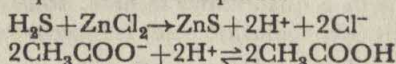
Notice that the added acetate ions react with the hydrogen ions to produce acetic acid, and the solution now contains a buffer of acetic and sodium acetate.

Table 11.8   Some Buffer Solutions with their pH values
at 25°C

Buffer solution	pH
0·1 M poassium tetroxalate	1·48
0·05 M potassium hydrogen phthalate	4·01
0·01 M acetic acid+0·01 M sodium acetate	4·70
0·01 M Na$_2$HPO$_4$+0·01 M KH$_2$PO$_4$	6·85
0·05 M Borax	9·18
0·025 M NaHCO$_3$+0·025 M Na$_2$CO$_3$	10·00

This buffer resists a change in the pH of the solution. Table 11.8 gives the composition and pH values of some buffer solutions.

*Experimental determination of pH is described in Chapter 12.

11.5.7 Titration of Acids and Bases

When an acid and a base are mixed in equimolar amounts in water, we expect the following reaction:

$$HA + H_2O \rightarrow H_3O^+ + A^-(aq)$$
$$B + H_2O \rightarrow BH(aq)^+ + OH^-(aq)$$

Adding, $$HA + B \xrightarrow{H_2O} H_3O^+ + A^- + BH^+ + OH^-$$
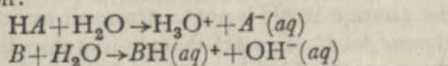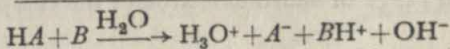
If the acid HA and the base B have high degrees of ionisation, then both A^- and BH^+ are weak conjugates. The net ionic reaction will then be,

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

For example, the reaction

$$Na^+ OH^- + H^+ Cl^- \rightarrow H_2O + Na^+ Cl^-$$
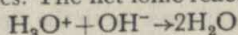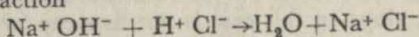
reduces to a combination of the hydrogen ion with the hydroxide ion to yield water. Thus, when an acid and base react in water, the net ionic reaction reduces to the ionisation equilibrium of water and the formation of a salt. We say that the acid and the base neutralise each other; and the pH of the resultant solution will be the pH of water, or $7 \cdot 0$. The combination of H_3O^+ with OH^- forms the basis of the technique called *acid-base titration*, i.e. the progressive addition of one reactant to the other.

Titration of a strong acid and strong base: When we add a solution of a base to that of an acid, the pH will progressively increase. The hydroxide ions from the base will react with the H_3O^+ of the acid to yield water, thus depleting

Volume of NaOH added (ml)⟶
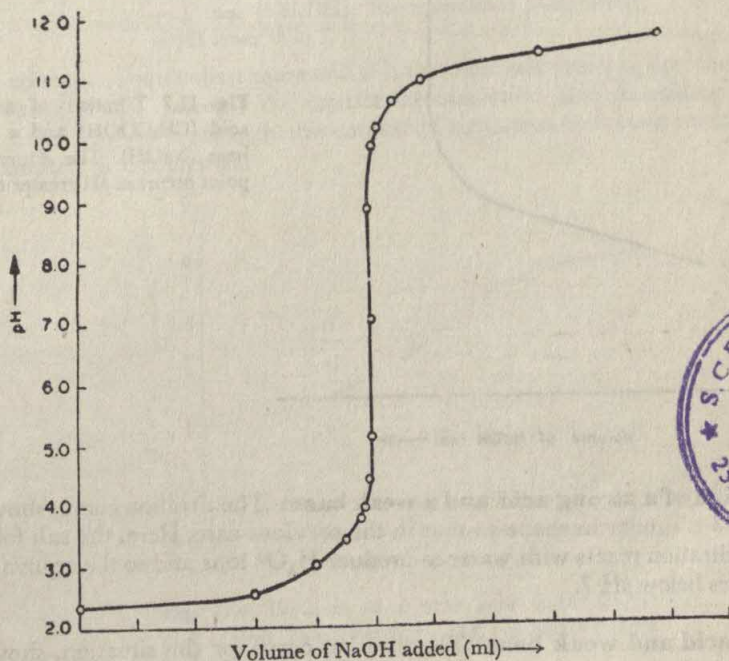
Fig. 11.1 Titration of a strong acid (HCl) and a strong base (NaOH). Equivalence point occurs at the midpoint of the curve at $pH = 7 \cdot 00$.

the concentration of H_3O^+. At the neutralisation point, all the acid is consumed by the base and the pH will be 7·0. Further addition of base will make the solution basic and the pH will increase beyond 7·0. Initially, and also at the end of the titration, the change in pH is not as dramatic as near the neutralisation point (also called the *end point*). The pH sharply increases from about 4 to about 10 within a 0·2 ml range of added base around the end point. The pH at the point is 7·00.

Titration of a weak acid and a strong base: Fig. 11.2 shows the titration curve obtained when acetic acid reacts with the strong base, sodium hydroxide. Again, the maximum variation in the pH value occurs around the equivalence point. However, the slope in this case is not as steep as in the strong acid–strong base titration curve. This is due to the fact that the sodium acetate formed in the reaction reacts with water to yield hydroxide ions, thus decreasing the H_3O^+ ion concentration. Hence the equivalence point in these situations lies at a pH higher than 7.
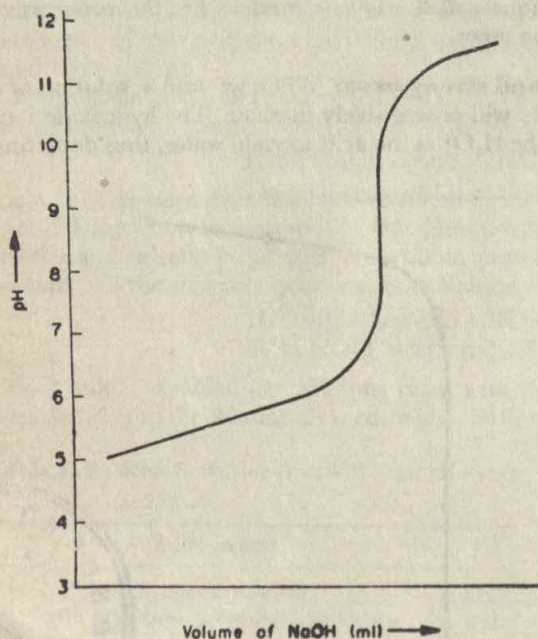
Fig. 11.2 Titration of a weak acid (CH_3COOH) and a strong base ($NaOH$). The equivalence point occurs at pH greater than 7.

Volume of NaOH (ml) ──▶

Titration of a strong acid and a weak base: The titration curve, shown in Fig. 11.3 is similar in shape to that in the previous case. Here, the salt formed in the titration reacts with water to produce H_3O^+ ions and so the equivalence point lies below pH 7.

Weak acid and weak base: The titration curve for this situation, shown in Fig. 11.4, displays no sharp changes in pH as the titration proceeds. The weak acid and its salt, as well as the weak base and its salt together form an efficient buffer system, making the observation of the end point difficult.

11.5.8 Equivalent Mass and Normality in Acid–Base Reactions

A convenient way of expressing the concentration of a solute in a solvent is by specifying the *normality* of the solution. The definition of normality is based on
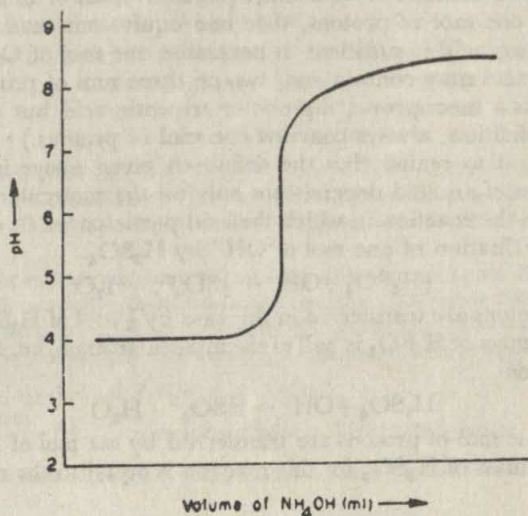
Fig. 11.3 Titration of a strong acid (HCl) and a weak base (NH₄OH). The equivalence point occurs at pH lower than 7.

the concept of equivalent mass and it is therefore necessary to first consider the meaning of this concept. We restrict the discussion here to acids and bases; the extension of the idea, in the context of oxidation-reduction reactions, will be treated in Chapter 12.
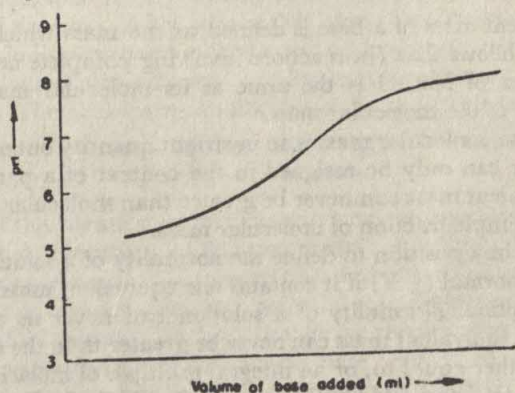
Fig. 11.4 Titration of a weak acid (CH₃COOH) and a weak base (NH₄OH). The equivalence point is ill-defined.

We know that one mol of OH^- can be neutralised by one mol of HCl. However, one mol of OH^- require only half a mol of H_2SO_4 for neutralisation.

This means that as far as neutralisation of one mole of OH^- is concerned, a mol of HCl (36·5 g of HCl) and half a mol of H_2SO_4 (49·0 g of H_2SO_4) are *equivalent*; the equivalence arising from the fact that in each case one mol of protons (H_3O^+ ions) are available. If we define equivalent mass of an acid as the mass which *transfers* one mol of protons, then one equivalent mass (or simply one equivalent) of *any* acid is sufficient to neutralise one mol of OH^-. (Note that one *mol* of an acid may contain one, two or three mol of protons depending on whether it is a monoprotic, diprotic or triprotic acid but one *equivalent* of an acid, by definition, always contains one mol of protons.)

It is important to realise that the definition given above implies that the equivalent mass of an acid depends not only on the molecular formula of the acid but *also* on the reaction in which the acid participates. Consider again the complete neutralisation of one mol of OH^- by H_2SO_4.

$$\tfrac{1}{2}H_2SO_4 + OH^- \rightarrow \tfrac{1}{2}SO_4^{2-} + H_2O$$
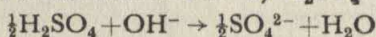
One mol of protons are transferred in this case by $\tfrac{1}{2}$ mol of H_2SO_4. Therefore, the equivalent mass of H_2SO_4 is half of the molecular mass, i.e. 49·0 g. Consider now the reaction

$$H_2SO_4 + OH^- \rightarrow HSO_4^- + H_2O$$
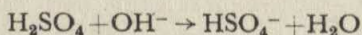
In this case, one mol of protons are transferred by *one* mol of H_2SO_4. Hence, the equivalent mass of H_2SO_4 for this reaction is equal to the molecular mass, i.e. 98·0 g.

Example 11.12 Calculate the equivalent mass of H_3PO_4 in each of the following reactions.

$$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$$
$$H_3PO_4 + 2OH^- \rightarrow HPO_4^{2-} + 2H_2O$$
$$H_3PO_4 + 3OH^- \rightarrow PO_4^{3-} + 3H_2O$$
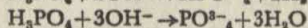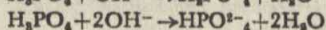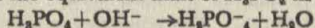
In the first reaction, one mol of protons are transferred by one mol of H_3PO_4. The equivalent mass of H_3PO_4 is, therefore, equal to its molecular mass (98·0 g). In the second and third reactions, the equivalent mass is, respectively, 49·0 g (98·0/2) and 32·67 g (98·0/3).

The equivalent mass of a base is defined as the mass which *accepts* one mol of protons. If follows that (in reactions involving complete neutralisation) the equivalent mass of NaOH is the same as its molecular mass while that of $Al(OH)_3$ is 1/3 of the molecular mass.

To summarise, molecular mass is an invariant quantity but equivalent mass is not. The latter can only be assigned in the context of a particular reaction. Further, equivalent mass can never be greater than molecular mass. It is either equal to, or a simple fraction of molecular mass.

We are now in a position to define the normality of a solution. A solution is said to be one normal (1 N) if it contains one equivalent mass of the solute per litre of the solution. Normality of a solution can never be smaller than the molarity (since equivalent mass can never be greater than the molecular mass). Usually it is either equal to, or an integral multiple of molarity. For example, 1 M HCl=1 N HCl and 1 M $Ca(OH)_2$=2 N $Ca(OH)_2$. It should be understood that normality, like molarity, is a measure of concentration; it has no connection with the strength or weakness of an acid or base.

The use of normality is particularly convenient in acid-base titrations for the following reason. We know that V_1 ml of an acid of normality N_1 contains $V_1 N_1 / 1000$ equivalents of the acid. Similarly, V_2 ml of a base of normality N_2,

contains $V_2 N_2/1000$ equivalents of the base. If the two solutions exactly neutralise each other, then the number of equivalents of the acid must be equal to the number of equivalents of the base, i.e.

$$N_1 V_1 = N_2 V_2$$

V_1 and V_2 can be obtained from observing the end point in a titration. Hence, if the normality of one of the solutions is known, that of the other can be calculated.

Example 11.13 0·63 g of oxalic acid, $(COOH)_2$, are present in 100 ml of a solution. 10·0 ml of this solution can be neutralised by 5·0 ml of a sodium hydroxide solution. Calculate the normality of the sodium hydroxide solution. What is the concentration of NaOH in the solution?

Since 0·63 g of oxalic acid are present in 100 ml, 6·3 g are present in 1 litre. The equivalent mass of oxalic acid in this case is 63 g (half of the molecular mass). Therefore, 1/10 of the equivalent mass is present in the solution, i.e. the normality of oxalic acid solution $= 1/10 \, N = 0·1 \, N$. To find normality of the sodium hydroxide solution, we use the relation $N_1 V_1 = N_1 V_2$.

Now, $N_1 = 0·1 \, N$, $V_1 = 10·0$ ml, $V_2 = 5·0$ ml and $N_2 = ?$

$$N_2 = \frac{0·1 \times 10·0}{5.0} = 0·2 \; N = \text{normality of sodium hydroxide solution}$$

Since the equivalent mass of NaOH is 40·0 g concentration of NaOH $= 40·0 \times 0·2 = 8·0$ g litre^{-1}.

11.5.9 Indicators

During the titration of an acid with a base, the detection of the end point is achieved by using a class of coloured compounds called *indicators*. Indicators are weak acids or bases (such as vegetable dyes and litmus) which have different colours in their acid forms and basic forms. For example, the compound methyl orange is a weak base that has an orange colour in its acid form and a yellow colour in the conjugate base form. When an acid is added to a solution of a base, with methyl orange as an indicator, the acid first reacts with the OH^- of the base. After all the OH^- ions are consumed by the acid (end point), the indicator reacts with the acid and changes to its acid form. At this point, the colour of the indicator, and hence of the solution, changes from yellow to orange. The acid–base equilibrium of the indicator is written as

$$In^- + H_3O^+ \rightleftharpoons HIn + H_2O$$
<div style="text-align:center">YELLOW   ORANGE</div>
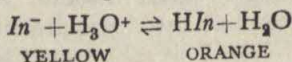
The end point of the titration is thus detected by the change in colour. The pK value of methyl orange is 3·7. This means that at a pH of 3·7 both the In^- and the HIn forms are equal in concentration and the solution colour will be between yellow and orange. An end point in the pH range of 3·7 can be detected by methyl orange. Methyl orange is thus a good indicator for titrations involving a strong acid and a weak base (Fig. 11.4).

Indicators, such as phenolphthalein, display a change in colour upon addition of OH^- ions as follows:

$$HIn + OH^- \rightleftharpoons In^- + H_2O$$
<div style="text-align:center">NO COLOUR   PINK</div>
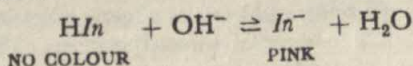
The pK value of phenolphthalein is 9·1 and it is a good indicator for titrations involving weak acids and strong bases where the end point occurs in the pH

Table 11.9 Some Acid–Base Indicators

Indicator	pK	pH range	Colour	
			in acid	in base
Thymol blue (acid)	1·7	1·2 – 2·8	Red	Yellow
Methyl orange	3·7	3·1 – 4·4	Red	Yellow
Methyl red	5·1	4·3 – 6·1	Red	Yellow
Litmus	6·5	5·5 – 7·5	Red	Blue
Phenol red	7·8	6·8 – 8·4	Yellow	Red
Thymol blue (base)	8·8	8·0 – 9·6	Yellow	Blue
Phenolphthalein	9·1	8·0 – 10·0	Colourless	Pink
Alizarin yellow	11·0	10·1 – 12·6	Yellow	Violet

range 8·0–10·0 (see Fig. 11.2). Table 11.9 lists several indicators that are commonly used for determining end points in acid–base titrations.

11.5.10 Acid–Base Equilibria in Non-aqueous Solvents

We have been considering so far acid–base equilibria in aqueous solutions. The solvent water itself behaves as a Brönsted base towards an acid and as an acid towards bases dissolved in it. This behaviour has the consequence that all acids stronger than water yield H_3O^+ in water, or acids much stronger than water appear equally strong in aqueous solution. To distinguish between strengths of these acids, one will have to use a solvent that is a weaker Brönsted base than water.

The Brönsted theory of proton transfer is applicable to other solvent media. For example, if we use liquid ammonia as a solvent, we will have the reactions,

$$HA + NH_3 \rightleftharpoons NH^+_4 + A^-$$
$$\text{and} \quad B + NH_3 \rightleftharpoons NH^-_2 + BH^+$$
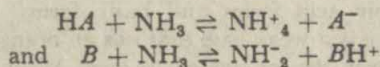
Like water, ammonia exhibits an auto-ionisation equilibrium:

$$NH_3 + NH_3 \rightleftharpoons NH^-_2 + NH^+_4$$
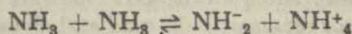
Thus one obtains the salts of ammonia, NH_4Cl and KNH_2. The latter is the analogue, in liquid ammonia, of KOH in water.

We have already mentioned the use of glacial acetic acid as a solvent to study acid strengths (section 11.5.3). This solvent acts as a Brönsted base towards stronger acids like hydrochloric acid.

$$HCl + CH_3COOH \rightleftharpoons CH_3COOH^+_2 + Cl^-$$
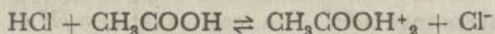
Other solvents used are sulphuric acid, amides and liquid sulphur dioxide. The determination of the strengths of acids and bases in these solvents, and in solvent mixtures, has been a subject of intensive study in recent years.

11.5.11 Lewis Acids and Bases

The Brönsted concept of acids and bases is a generalisation of the Arrhenius idea and is applicable to a variety of solvent systems. The emphasis on the proton or the hydrogen ion is a basic tenet of the Bronsted theory. In 1923, G. N. Lewis suggested an even more generalised idea of acids and bases, wherein the case of protons becomes a particular example. Look at any Bronsted

base (OH^-, SO^{2-}_4, CH_3COO^-). All these compounds are electron-rich, containing at least one lone pair of electrons that are available for donation or transfer. Whenever a Brönsted base is neutralised, its electron pair is donated. Similarly, every Brönsted acid is electron-deficient and accepts an electron pair (H^+ is a specific example). In a Brönsted acid-base reaction such as

$$H_3O^+ + CH_3COO^- \rightleftharpoons CH_3COOH + H_2O$$
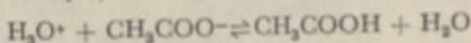
the acid and its conjugate base differ essentially in the availability of an electron pair.

Lewis noted this generality and defined an acid as an ion, atom, or molecule that accepts an electron pair, and a base as one that donates an electron pair. An acid-base pair may then also be defined as a donor-acceptor pair. The generalised acid-base situation can thus be written as

$$A+ \ : B \rightarrow A : B$$
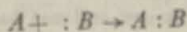
In this general equation, A is called the Lewis acid, defined as an electron acceptor and B, the Lewis base, is the electron donor. The species $A : B$ may then be variously called a coordination compound, donor-acceptor complex, acid-base, etc. A Lewis acid, A, may then be a positive ion or an electron deficient molecule. A Lewis base B, would be any anion molecule with a lone pair or a molecule with a double bond. A typical Lewis acid-Lewis base complex $BF_3:NH_3$ was discussed earlier (section 4.5.7).

In coordination compounds, B (the Lewis base) is termed a ligand and A (the Lewis acid) is the central metal ion. In organic chemical reactions, A is an electrophile while B is the nucleophile. In fact, all metal ions or atoms are Lewis acids. They are usually found coordinated to several Lewis bases or ligands. When a salt such as sodium chloride is dissolved in water, the hydration of the cation, $[Na(H_2O)_6]^+$ is a Lewis acid-base interaction, where water is the Lewis base that donates lone pairs to the ion. The hydrated anion, $[Cl(H_2O)^-_x]$ is a hydrogen-bonded complex in which water molecules are Lewis acids.

Carbonium ions are Lewis acids and carbanions (see Chapter 14) are Lewis bases. Even if the species are not long-lived or stable (e.g. carbonium ions like CH^+_3), conceptually it is proper to call them as acids. In cases of this kind, we may write the general equation,

$$A : B' + A' : B \rightarrow A : B + A' : 'B'$$
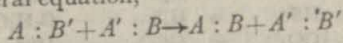
In solution, A' and B' could be solvent molecules. Thus, charge-transfer, hydrogen bonding, ion-dipole interaction, complexation, and indeed *every chemical reaction may be viewed as an example of the interaction between a Lewis acid and Lewis base*. The interaction energy is what classifies reactions as ionic, charge-transfer, bond formation and so on. Rules have now been developed concerning the stability and mechanisms of the reactions of the type discussed above. Classification of the strengths of generalized acids and bases on the grounds of polarisability and electronegativity has given birth to the ideas of hard and soft acids and hard and soft bases. A detailed discussion of this idea would, however, be beyond the scope of this book.

SUGGESTED READING

C. A. VanderWerf, *Acids, Bases, and the Chemistry of the Covalent Bond*, Reinhold Publishing Corporation, New York, 1961.

PROBLEMS

11.1   It is often stated that in aqueous solution proton is unstable as an isolated entity and exists as H_3O^+. Give evidence in support of this statement. Can it also exist as $(H_3O^+)(H_2O)_n$, where n may be 1, 2, 3, 4,...?

11.2   (*i*) What do you understand by the 'levelling effect' of a solvent? Elaborate on the statement: 'The strongest base and the strongest acid that can exist in water are OH^- and H_3O^+, respectively.'

(*ii*) What are the strongest base and acid respectively that can exist in (*a*) liquid NH_3 and (*b*) pure alcohol. CH_3CH_2OH?

(*iii*) Generalise about the strongest acid and base that can exist in any self-ionising solvent.

11.3   (*i*) What is the conjugate base of: (*a*) H_3PO_4, (*b*) $H_2PO_4^-$, (*c*) NH_3, (*d*) HS^-, (*e*) H_3O^+, (*f*) $HOCl$, (*g*) $Al(H_2O)^{3+}{}_6$, (*h*) methyl alcohol, CH_3OH, (*i*) phenol, and (*j*) OH^-.

(*ii*) What is the conjugate acid of: (*a*) F^-, (*b*) OH^-, (*c*) $PO^{3-}{}_4$, (*d*) NH_3, (*e*) NH_2^-, (*f*) HS^-, (*g*) SO_4^{2-}, (*h*) CH_3OH, (*i*) HGO_a^-, and (*j*) aniline.

11.4   (*i*) Each of the following reactions is displaced to the right. Arrange all the Brönsted acids that appear in these equations in order of decreasing acid strength. Make a similar list for the Brönsted bases.

(*a*) H_3O^+ + H_2PO_4 → H_3PO_4 + H_2O

(*b*) HCN + OH^- → H_2O + CN^-

(*c*) H_3PO_4 + CN^- → HCN + $H_2PO_4^-$

(*d*) H_2O + NH_2^- → NH_3 + OH^-

(*ii*) Based upon knowledge about the relative strength of the acids obtained in (*i*) would you expect an appreciable reaction (i.e. over 50 per cent) to occur in the following (complete the reaction yourself):

(*a*) H_3O^+ + CN^- →

(*b*) NH_3 + CN^- →

(*c*) HCN + $H_2PO_4^-$ →

(*d*) H_3PO_4 + NH_2 →

11.5   (*i*) Each of the following reactions, is displaced to the right. Arrange all the Brönsted acids that appear in these equations in order of decreasing acid strength. Make a similar list for the Brönsted bases.

(*a*) HCO_3^- + OH^- → H_2O + CO_3^{2-}

(*b*) $HC_2H_3O_2$ + HS^- → H_2S + $C_2H_3O_2$

(*c*) H_2S + CO_3^{2-} → HCO_3^- + HS^-

(*d*) HSO_4^- + $C_2H_3O_2$ → $HC_2H_3O_2$ + SO_4^{2-}

(*ii*) Based upon knowledge obtained in (*i*) about the strength of the acids and bases, would you expect an appreciable reaction (i.e. over 50 per cent) to occur in the following (write down the complete reaction yourself):

(*a*) HCO_3^- + $C_2H_3O_2^-$ →

(*b*) HSO_4^- + HS^- →

(*c*) $HC_2H_3O_2$ + CO_3^{2-} →

(*d*) H_2S + $C_2H_3O_2^{2-}$ →

11.6   Which compound of each of the following pairs is the stronger acid and why?

(*i*) H_3PO_4 or H_3AsO_4, (*ii*) H_3ASO_3 or H_3AsO_4,

(*iii*) H_2SO_4 or H_2SO_3, (*iv*) H_3BO_3 or H_2CO_3, (*v*) H_2Se or HBr

11.7   Which compound of each of the following pairs is the stronger base and why?

(*i*) P^{3-} or S^{2-}, (*ii*) PH_3 or NH_3, (*iii*) SiO_3^{2-} or SO_3^{2-} (*iv*) NO_2^- or NO_3^-, (*v*) Br^- or F^-

11.8 Perchloric acid, $HClO_4$, is a stronger acid than chloric acid, $HClO_3$. On the other hand, periodic acid, H_5IO_6, is a weaker acid than iodic acid, HIO_3. Draw Lewis structures for the four compounds and explain the differences in acid strength of the acids.
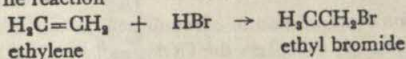
11.9 (i) The reaction
$$H_2C=CH_2 \;+\; HBr \;\rightarrow\; H_3CCH_2Br$$
$$\text{ethylene} \qquad\qquad \text{ethyl bromide}$$
can be considered to occur in two steps:
$$H_2C=CH_2 + HBr \;\longrightarrow\; H_3C-CH^+_2 + Br^-$$
$$H_3C-CH^+_2 + Br^- \;\longrightarrow\; H_3C-CH_2Br$$
Each step is an acid-base reaction. Label all acids and bases.
(ii) Acetylene, $HC \equiv CH$, does not react with OH^-, but reacts with $NaNH_2$ in liquid NH_3. When ammonia is allowed to evaporate, the residue is found to be sodium acetylide, $HC \equiv C : Na^+$, a typical ionic solid. When the experiment is repeated with ethylene, $H_2C=CH_2$, the residue is unreacted sodium amide.
(a) Write down the reaction between acetylene and $NaNH_2$ in liquid NH_3. Label all acids and bases.
(b) Why does this reaction not take place in aqueous medium?
(c) Explain why ethylene does not react with $NaNH_2$ in liquid NH_3 whereas acetylene does.
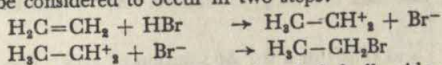
11.10 Calculate the $[H^+]$, $[OH^-]$, pH and pOH values missing from the following table. Assume that the aqueous solution is at 25°C.

	$[H^+]$	$[OH^-]$	pH	pOH
(a)	?	5.0×10^{-13}	1.7	12.3
(b)	1.6×10^{-8}	6.3×10^{-7}	?	6.2
(c)	?	2.8×10^{-11}	3.4	10.6
(d)	5.0×10^{-2}	2.0×10^{-13}	1.3	?
(e)	?	1.4×10^{-3}	11.1	2.9
(f)	5.0×10^{-3}	2.0×10^{-12}	?	11.7
(g)	1.0×10^{-13}	1.0×10^{-1}	13.0	?
(h)	1.1×10^{-13}	?	13.0	1.0
(i)	1.2×10^{-9}	?	8.9	5.1
(j)	1.3×10^{-5}	?	?	?

11.11 At 25°C, the degree of ionisation of water is found to be 1.8×10^{-9}. Calculate the ionisation constant and the ionic product of water at this temperature.

11.12 At 25°C, the degree of ionisation for water is 1.8×10^{-9}. How is this affected in presence of 10^{-8} M HCl (assume complete ionisation for the acid)? What is the pH of the solution?

11.13 The dissociation constant of acetic acid is 1.8×10^{-5}. Calculate the degree of dissociation and hydrogen ion concentration in (a) 0.25 N acetic acid solution and (b) 0.25 N acetic acid solution containing 0.25 N sodium acetate if the sodium acetate is completely dissociated.

11.14 4.0 g of NaOH are dissloved ; in one litre of a solution containing one mol each of acetic acid and sodium acetate. What will be the pH of the resulting solution? ($K_a=1.8\times 10^{-5}$ for acetic acid)

11.15 Find the concentration of OH^- ions in a solution of 0.2 M in NH_4OH and 0.4 M in NH_4Cl. ($K_{NH_4OH}=1.8\times 10^{-5}$)

11.16 The pH of 0.02 M of a weak base, BOH is 10.45. Calculate the pH of the solution formed by mixing 100 ml of a 0.02 M of the weak base with 10.0 ml of 0.1 M HCl.

11.17 It is found that 0.1 M solution of three sodium salts NaX, NaY and NaZ have pH values of 7.0, 9.0 and 11.0 respectively. Arrange the acids in order of increasing strength. Where possible, calculate the ionisation constants of the acids.

11.18 (*i*) Calculate the pH of a buffer (A_1) which is 0.01 M in acetic acid and 0.010 M in sodium acetate, and a buffer (A_2) which is 0.1 M in acetic acid and 0.1 M in sodium acetate. (*ii*) Calculate the pH when 1.0×10^{-3} mol of HCl is added to one litre of the buffer A_1 and the same quantity of HCl is added to one litre of buffer A_2.

11.19 At 25°C and 1 atm, the saturation concentration of carbonic acid in water is 0.034 M. (*a*) Calculate the pH of the solution. (*b*) Calculate the CO^{2-}_3 molarity. (*c*) If 0.2 mol of HCl is added to 1 litre; calculate the CO_3^{2-} molarity. ($K_1 = 4.5 \times 10^{-7}$ and $K_2 = 4.7 \times 10^{-11}$)

11.20 What are [H$^+$], [HS$^-$], [S^{2-}] and [H$_2$S] in a 0.1 M solution of H$_2$S? The two dissociation constants of H$_2$S are $K_1 = 1.1 \times 10^{-7}$ and $K_2 = 1.0 \times 10^{-14}$.

11.21 What is an acid-base indicator? What type of indicator will you employ in titration of (*a*) strong acid and strong base, (*b*) strong acid and weak base, (*c*) weak acid and strong base, and (*d*) weak acid and weak base. Give reasons.

11.22 Ionisation constants of phenolphthalein and methyl red are 2×10^{-10} and 5×10^{-6}. What fraction of each will be red at a pH of 7?

11.23 If the solubility product of Ag$_2$C$_2$O$_4$ is 1×10^{-11} calculate the weight of Ag$_2$C$_2$O$_4$ in 2.5 litres of a saturated solution.

11.24 Hydrogen sulphide is bubbled into a 0.2 M NaCN solution which is 0.02 M in each [Ag(CN)$_2$]$^-$ and [Cd(CN)$_4$]$^{2-}$. Determine which sulphide precipitates first. The values of K_{sp} for HgS and CdS are 1×10^{-50} and 7.1×10^{-28} respectively.

11.25 To a solution that contains 0.1 M Ca^{2+} and 0.1 M Ba^{2+}, sodium sulphate solution is added slowly. The solubility products of CaSO$_4$ and BaSO$_4$ are 2.4×10^{-5} and 1.1×10^{-10} respectively. What is the sulphate ion concentration at the instant when the first solid precipitates? What is that solid? Neglect dilution and calculate the barium ion concentration present when CaSO$_4$ precipitation occurs.

11.26 Explain the following observations:

(*a*) A solution made by adding 1 mol of sodium acetate and 1 mol of hydrochloric acid to 1 litre of water has the same pH as a solution made by dissolving 1 mol of acetic acid to 1 litre of water.

(*b*) Magnesium hydroxide is soluble in a solution of ammonium chloride, but not in sodium or potassium chloride solutions.

(*c*) Cadmium sulphide is not precipitated when hydrogen sulphide is passed through cadmium chloride in strong acid solution.

(*d*) Methyl orange is not a suitable indicator when oxalic acid is titrated against caustic soda solution.

(*e*) The precipitation of magnesium hydroxide by NH$_4$OH is prevented by the addition of NH$_4$Cl but its precipitation by NaOH is not prevented by the addition of NaCl.

(*f*) Zinc sulphide is precipitated by hydrogen sulphide from an ammoniacal solution, but not from a strong hydrochloric acid solution.

(*g*) Calcium oxalate is soluble in HCl although it is almost insoluble in acetic acid.

(*h*) A white precipitate is formed when concentrated hydrochloric acid is added to concentrated barium chloride solution although barium chloride is not as insoluble as AgCl or Hg$_2$Cl$_2$ or PbCl$_2$.

(*i*) Lead sulphate dissolves in ammonium acetate.

11.27 Identify the Lewis acids and Lewis bases in the following: AlCl$_3$, I$_2$, Na, Na$^+$, PtCl$^{2-}_6$, (CH$_3$)$_3$C$^+$, BF$_3$, NH$_3$, H$_3$C—C$_6$H$_4$—SO$^-_3$, and [Co(H$_2$O)$_6$]$^{3+}$.

11.28 In the following cases, which are the Lewis acids and which are the Lewis bases? Li(H$_4$O)$^+_6$, Li(HCONH$_2$)$^+_6$, C$_6$H$_6$: I$_2$, (H$_2$O)$_2$, and [R$_2$—C⁺OH   HSO$^-_4$].
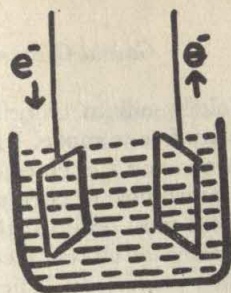
12

Electrochemistry

Davy supposes that there are two kinds of electricity, with one or other of which all bodies are united. These we distinguish by the names of positive and negative electricity....But whether the hypothesis be altogether founded on truth or not, it is impossible to question the great influence of electricity in chemical combinations.

JANEK MARCET

...all the facts show us...that the electric current is only another form of the forces of chemical affinity...that, in other words, the forces termed chemical affinity and electricity are one and the same.

MICHAEL FARADAY

As early as 1760, Henry Cavendish investigated the conduction of electricity by solutions of salts in water. This was later explored in greater detail by Davy, Faraday, Arrhenius, and Ostwald, who systematised the science of *electrochemistry*. This area deals with a study of electrical transport and interconversion of electrical and chemical energy by chemical substances.

12.1 ELECTRICAL CONDUCTION

Electrical energy may be transported through substances by the *conduction* of electric charges from one place to another. A metal rod conducts electricity because of the motion of the loosely held 'conduction' electrons (see Chapter 7), under the application of an electrical field. The metal nuclei are rigidly held in the solid and therefore they do not move under the applied field. However, the loosely held electrons can easily migrate and carry the current. A sustained flow of charge in a wire can occur if we add electrons to one end of the rod and remove them from the other end (by a direct current, or a dc source), thereby maintaining electrical neutrality everywhere and causing the current to flow.

As opposed to metallic conduction, where only electrons are the charge carriers, salt solutions conduct by the migration of ions in the medium. A crystal of sodium chloride conducts electricity inefficiently since the ions are held tightly to the lattice; the conduction is mainly due to the movement of

399

ions through the vacancies present in the crystal. Molten sodium chloride however, is a far superior conductor since here, the ions are free to move. The positive sodium ions migrate towards the negative electrode and the chloride ions towards the positive electrode. In order to get a sustained flow of current, and not an accumulation of ions at the electrodes, reactions must occur at the electrodes so as to maintain electrical neutrality. The external circuit feeds electrons into the medium at the negative electrode (called the *cathode*). These will be consumed by the positive ions (termed *cations* since they migrate to the cathode), and released at the *positive* electrode (called the *anode*) by the *negative ions* (termed *anions*) of the medium. Thus, in contrast to the case of conduction by metals, one would expect reactions to occur between electrons and ions whenever dc electrical conduction is mediated through ions in a medium.

12.2 ELECTROLYSIS

12.2.1 Half-cell Reactions

Let us examine the electrical circuit shown in Fig. 12.1. We have a dc battery which sends an electric current through the conducting medium, which in this case is molten sodium chloride. Electrons enter the melt from the battery at the cathode, and when the circuit is complete, they leave the melt at the anode returning to the battery. In order to maintain electrical neutrality throughout the cell, and to maintain the current, reactions must occur at the two electrodes. At the cathode, sodium ions from the medium combine with the electrons available to produce sodium metal which accumulates at the cathode region: $Na^+ + e^- \rightarrow Na$. (Here and elsewhere an electron is donated by the symbol e^- to facilitate charge balancing.)

During this reaction, mass and charge are both conserved. The reaction itself may be seen to be the reverse of ionisation, and hence the energy involved in the reaction would be roughly of the order of the ionisation energy of sodium (5·1 ev or 117·3 kcal mol^{-1}). Since ionisation of sodium atom is endothermic, the cathode reaction between sodium ion and the electron will be exothermic, and therefore expected to be favourable. *Such reactions which involve the addition of electrons are defined as reduction reactions.* Accordingly, we say that sodium ions are reduced to sodium atoms at the *cathode*. At the same time, chloride ions migrate towards the anode and are oxidised to chlorine at the anode:
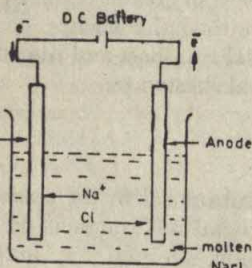
Fig. 12.1 An electrolysis cell

$$Cl^- \rightarrow \tfrac{1}{2}Cl_2 + e^-$$
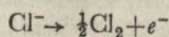
This is an oxidation reaction since in this reaction, electrons are released. Chloride ions are oxidised to chlorine gas which can escape from the anode. The anode reaction is the reverse of an electron-affinity process, and for chlorine this reaction at the anode is endothermic to the extent of about 80 kcal mol^{-1}. Overall, the reaction occurring in the vessel is an *oxidation-reduction* (*redox* for short) reaction, made up of two *half-reactions*:

CATHODE : reduction $Na^+ + e^- \rightarrow Na$
ANODE : oxidation $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$
NET REACTION $\overline{Na^+ + Cl^- \rightarrow Na + \frac{1}{2}Cl_2}$
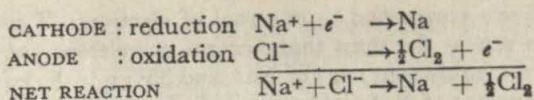
We have seen that the passage of direct current through molten sodium chloride, results in the formation of the elements sodium and chlorine. Such a reaction mediated by the consumption of electrical energy, is called *electrolysis*, and the apparatus depicted in Fig. 12.1 is called an *electrolysis cell*. An electrolysis reaction is a redox reaction comprising a reduction half-reaction involving the gain of electrons occurring at the cathode and an oxidation half-reaction involving loss of electrons at the anode. The noteworthy feature of electrolysis is that electrical energy is used to produce a chemical reaction. Electrolysis reactions may be accompanied by the liberation of heat as in the case of NaCl or they may be endothermic. The two half-reactions in electrolysis are referred to occasionally as *half-cell reactions*, since together they describe the overall reaction occurring in the cell.

Let us now consider the electrolysis of an aqueous solution of sodium chloride. The species that can undergo redox reactions are Na^+, Cl^-, and H_2O. At the anode, oxidation of Cl^- and H_2O can occur:

$$Cl^-(aq) \rightarrow \frac{1}{2}Cl_2(g) + e^-$$
$$6H_2O \rightarrow O_2(g) + 4H_3O^+ + 4e^-$$
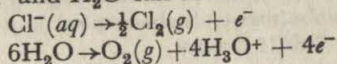
In dilute solutions, both reactions occur. The relative amounts of chlorine and oxygen released depend on the electrical voltage, current and temperature. In concentrated solutions, the product is essentially only chlorine gas.

At the cathode, reduction of Na^+ may occur to produce Na. Water may also be reduced to H_2.

$$Na^+ + e^- \rightarrow Na$$
$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$$
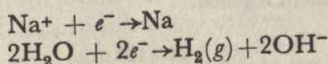
Both reactions are possible. However, in recent years it has been suspected that the second reaction occurs much more rapidly. (It is possible, though there has been no direct evidence for it, that the sodium metal formed by the first reaction reacts with water to yield H_2, Na^+ and OH^-.) Together then, the electrolysis reaction for aqueous NaCl is,

$$2NaCl + 2H_2O \rightarrow H_2(g) + Cl_2(g) + 2NaOH$$
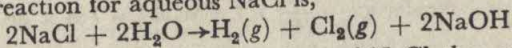
Electrolysing concentrated aqueous solutions of NaCl thus produces NaOH, H_2 and Cl_2. In dilute solutions, the reaction produces O_2 as well.

12.2.2 Faraday's Laws of Electrolysis

The quantitative relationship between the amount of electricity passed through a cell and the amount of substances of appearing or disappearing at the electrodes, is expressed by Faraday's laws of electrolysis (see section 3.2.1). As stated earlier, these laws suggested the electrical nature of matter and the particulate character of electricity; both suggestions receiving confirmation with the discovery and characterisation of electron, several decades after Faraday's work. In the light of the later developments, it is possible to interpret the laws of electrolysis in a simple manner. Consider the observation that in the electrolysis of molten sodium chloride, 96,487 coulomb of electricity (i.e. one Faraday of electricity) yield 23 g of sodium at the cathode and 35·5 g of chlorine gas at the anode. What do these numbers signify? Since the charge on an electron is $1·6 \times 10^{-19}$ coulomb and since electricity is just transport of

electrons, 96,487 coulomb correspond to one mol of electrons. If we define equivalent mass of an ion as the mass that accepts or releases one mol of electrons, then 23 g is the equivalent mass of Na^+ and 35·5 g is the equivalent mass of Cl^-. One equivalent of Na^+ yields one mol of sodium and one equivalent of Cl^- yields $\frac{1}{2}$ mol of Cl_2 thus explaining the experimental facts. In other words, the essential content of Faraday's laws is that one equivalent of electricity yields one equivalent of matter.

The definition of equivalent mass given above in terms of electron transfer is reminiscent of the definition given for acids and bases in terms of proton transfer (see section 11.5.8). For an ion also, equivalent mass can be assigned only in the context of a particular reaction. For example, if Cu^{2+} is reduced to Cu^+ (transfer of one mol of electrons), the equivalent mass is 63·5 g but for the reduction $Cu^{2+}+2e^- \rightarrow Cu$, the equivalent mass is 31·8 g because two mol of electrons are transferred per mol of copper ions.

Example 12.1 How many grams of silver can be produced by the electrolysis of silver nitrate solution, when a current of 1 ampere is passed through the cell for 5 minutes?

Total amount of electricity passed in the cell in coulombs is given by 1 amp×5×60s
  $= 300$ amp s$=300$ coulombs (since coulomb$=$amp$\times$s)
  $= 300/96487$ Faraday $= 0·00311$ Faraday
The reaction in the cell is $Ag^+ + e^- \rightarrow Ag$ and involves one electron per mol of Ag^+. Since 1 Faraday will yield 1 mol of Ag (107·9 g Ag) the amount of silver deposited
  $=0·00311 \times 107·9=0·333$ g

Example 12.2 In an industrial electrolytic cell, it is desired to produce 36 kg of magnesium metal per hour. Calculate the current required.

Amount of magnesium produced per second $= \dfrac{36 \times 10^3}{60 \times 60} = 10$ g $= \dfrac{10}{24·3}$ mol

The equivalent mass of magnesium is half its molecular mass since the metal is divalent. Hence for every mol of magnesium we need 2 faradays of electricity. The amount of current needed for the production of $10/24·3$ mol of magnesium per second is, therefore,

$$= \frac{10}{24·3} \times 2 \text{ faraday s}^{-1} = \frac{10}{24·3} \times 2 \times 96,487 = 7·94 \times 10^4 \text{ amp}$$

12.2.3 Applications of Electrolysis

Electrolysis finds widespread applications in the manufacture of many metals such as Na, Mg, Al and a number of chemicals such as $NaOH$, Cl_2, H_2O_2, and
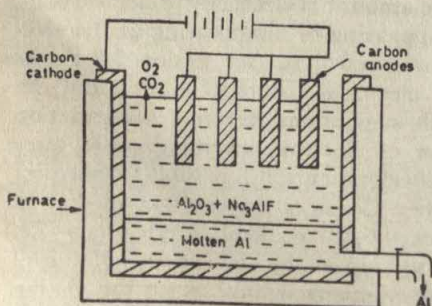
Fig. 12.2 Manufacture of aluminium by the Hall process. The anode reaction is $2O^{2-} + C \rightarrow CO_2 + 4e^-$. The cathode reaction is $Al^{3+} + 3e^- \rightarrow Al$.

$KMnO_4$. Fig. 12.2 shows the electrolysis cell used in the production of aluminium metal. In the laboratory, the preparation of ions in high oxidation states is often achieved electrolytically. In recent years, electro-organic chemistry has acquired importance in organic synthesis.

12.3 OXIDATION-REDUCTION REACTIONS

Oxidation-reduction reactions are by far the most important classes of reactions and occur ubiquitously, in electrolysis cells, in the human body, or in the environment around us. As mentioned before, an oxidation reaction involves loss of electrons, while a reduction reaction involves uptake of electrons. These two reactions occur together and hence the overall reaction is referred to as an oxidation-reduction, or a redox reaction. While the reactions cited in electrolytic cells involved changes in the charges of the individual species, redox reactions occur between covalent uncharged molecules as well, and in these cases the exchange of electrons is not obvious. Besides, there are atoms that display more than a single valence state. To keep track of the total number of electrons involved and to aid in the balancing of reactions, two methods are adopted as outlined below.

12.3.1 The Oxidation Number Concept

In the ionic molecule $NaCl$, the sodium atom transfers one electron to the chlorine. This leaves the sodium with a single positive charge as Na^+, and the chlorine with a negative charge as Cl^-. Na^+ can be reduced by an electron to yield an uncharged sodium atom. We refer to Na^+ as having an *oxidation number* of $+1$. The terms oxidation number and *oxidation state* refer to the same thing and are used synonymously. Similarly, Cl^- is referred to as being in the -1 oxidation state, or having an oxidation number of -1. The oxidation numbers of these ions obviously refer to the sign and number of charges on them. However, if we take the case of a molecule like H_2O, there is no complete transfer of electrons from hydrogen to oxygen. Since oxygen is more electronegative than hydrogen, the electrons comprising the O—H bond ' belong' more to oxygen than hydrogen. In other words, we may talk qualitatively of a ' formal charge ' on the atoms in covalent molecules. Thus, we may define the oxidation number of an atom as the charge which an atom *appears* to possess when electrons are counted according to some accepted rules. Electrons shared between two unlike atoms are counted to be with the more electronegative atom, and electrons between two like atoms are divided equally between the two. The oxidation numbers of hydrogen and oxygen in water are $+1$ and -2 respectively. This is because the hydrogen atoms in water appear to have lost one electron each, while oxygen atom appears to have gained two electrons, making its formal charge -2.

The oxidation numbers of H in H_2, Cl in Cl_2, or S in S_2 are all zero since electrons are shared between like atoms here.

The accepted rules for assignment of oxidation numbers are:

(1) All free elements shall be assigned the oxidation number of zero.
(2) When hydrogen is present in a compound, it will be assigned an oxidation number of $+1$ (except in hydrides, when it is -1).

(3) The sum of all oxidation numbers of the elements present in a compound will be zero.

(4) The sum of all oxidation numbers in a complex ion or a radical must equal the charge on the ion or the radical.

We notice from these rules that we have chosen hydrogen as our standard, from which we derive the oxidation numbers of other atoms. Sometimes as a corollary, it is stated that in compounds oxygen atom will always have an oxidation number of -2, except in peroxides where it is -1. The rules for assigning oxidation numbers by this scheme are consistent with the requirement of charge balance or the conservation of charge. But the oxidation numbers themselves do not denote actual charges on atoms, but rather 'formal charges', as mentioned earlier. For example, in P_2O_5 the oxidation number of oxygen is -2 and of phosphorous is $+5$. This does not mean that P_2O_5 consists of P^{5+} and O^{2-} ions. Rather, these numbers are arbitrarily assigned to atoms to help in balancing chemical equations with respect to stoichiometry and charge. It is not unusual to find strange values, such as zero or fractions, for oxidation numbers of atoms. In glucose, $C_6H_{12}O_6$, the oxidation number of carbon works out to zero. In $Na_2S_4O_6$ the oxidation number of sulphur is $+2 \cdot 5$.

Example 12.3 Calculate the oxidation numbers of each atom in the following.

(a) Cr_2O_3 (b) HNO_3 (c) HCl (d) ClO^{-1} (e) ClO^{-1}_2 (f) ClO^{-1}_3
(g) $HClO_4$ (h) H_3PO_3 (i) H_3PO_4 (j) $Na_2B_4O_7$ (k) Na_2O_2 (l) Pr_6O_{11}

Using the above rules, i.e. the oxidation number of oxygen is -2 and hydrogen is $+1$, we have

(a) total charge of the molecule is zero. Since each oxygen atom is -2, charge balance shows the oxidation number of each Cr to be $+3$. We may represent this as:

$$\underset{(2\times y)\ (3\times -2)}{Cr_2\ O_3} \qquad y=+3$$

(b)
$$\underset{+1\ \ y\ \ (2\times-2)}{H\ N\ O_3} \qquad y=+3 \qquad (c)\ \underset{+1\ \ y}{H\ Cl}\ \ y=-1$$

(d)
$$\underset{(y)\ \ (-2)}{Cl\ O^{-1}}\ \ y=+1 \qquad \text{(remembering the total charge is } -1)$$

(e)
$$\underset{y\ \ (2\times-2)}{Cl\ O^{-1}_2}\ \ y=+3 \qquad (f)\ \underset{y\ \ (3\times-2)}{Cl\ O_3^{-1}}\ \ y=+5 \qquad (g)\ \underset{+1\ \ y\ \ (4\times-2)}{H\ Cl\ O_4}\ \ y=+7$$

(h)
$$\underset{(+1\times3)\ \ y\ \ (3\times-2)}{H_3\ \ P\ \ O_3}\ \ y=+3 \qquad (i)\ \underset{(+1\times3)\ \ y\ \ (4\times-2)}{H_3\ \ P\ \ O_4}\ \ y=+5$$

(j)
$$\underset{(2\times+1)\ (4\times y)\ (7\times-2)}{Na_2\ \ B_4\ \ O_7}\ \ y=+3 \qquad (k)\ \underset{(2\times y)\ (2\times-1)}{Na_2\ \ O_2}\ \ y=1$$

(l)
$$\underset{(6\times y)\ \ (2\times11)}{Pr_6\ \ O_{11}}\ \ y=+22/6$$
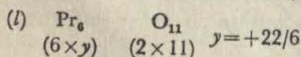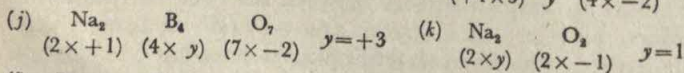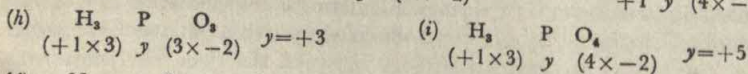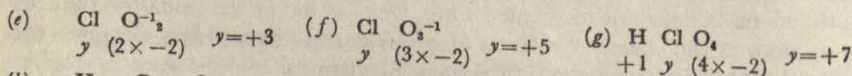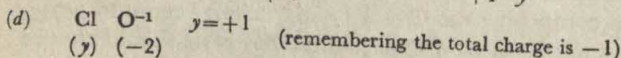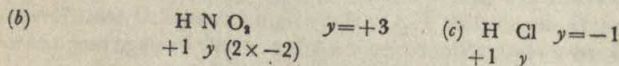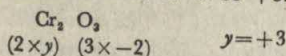
We define, in this formulation, *oxidation* as a chemical change in which there is an *increase in the oxidation number*, and *reduction* as a change involving a *decrease in the oxidation number*. An oxidising agent is a substance that does the oxidising, and in the process shows a decrease in its own oxidation number. A reducing agent does the reduction and in the process undergoes an increase in its own oxidation number. We shall clarify these points in the following example.

Example 12.4 Identify the oxidising a-d reducing agents and the atoms undergoing oxidation and reduction in the followings reactions:

$$(a)\quad H_2 + S \rightarrow H_2S$$
$$(b)\quad H_2SO_3 + 2H_2S \rightarrow 3S + 3H_2O$$
$$(c)\quad 2H^+ + Mg \rightarrow Mg^{2+} + H_2$$
$$(d)\quad H_2O_2 + H_2O_2 \rightarrow 2H_2O + O_2$$

(a) The oxidation numbers of hydrogen in H_2 and H_2S are zero and $+1$ respectively. Those of sulphur in S and H_2S are zero and -2 respectively. Hence the reaction involves oxidation of hydrogen and reduction of sulphur in going from left to right. H_2 is the reducing agent and S the oxiding agent.

(b) The oxidation numbers of hydrogen, sulphur and oxygen are denoted under the reagents:

$$H_2\ S\ O_3 + 2H_2\ S \rightarrow 3S + 3H_2\ O$$
$$+1\ +4\ -2\quad +1\ -2\quad\ 0\qquad\ +1\ -2$$
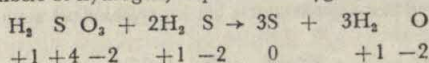
Oxygen does not undergo any change in its oxidation state. Neither does hydrogen. Sulphur in H_2SO_3 gets reduced to elemental sulphur ($+4$ to 0), while sulphur in H_2S gets oxidised from -2 to 0 in elemental sulphur. Hence H_2SO_3 is the oxidising agent and H_2S the reducing agent.

(c) $2H^+ + Mg \rightarrow Mg^{2+} + H_2$
$\quad\ \ +1\qquad 0\qquad +2\qquad 0$
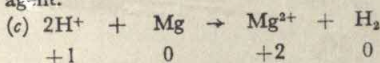
H is the oxidising agent which itself gets reduced ($+1$ to 0) and the reducing agent Mg gets oxidised (0 to $+2$).

(d) $H_2\ O_2 + H_2\ O_2 \rightarrow 2H_2O + O_2$
$\quad\ +1\ -1\quad +1\ -1\quad\ +1\ -2\quad\ 0$
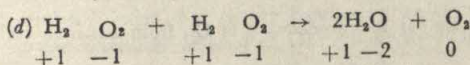
The oxidation number of oxygen in hydrogen peroxide, H_2O_2, is -1, in H_2O it is -2 and in O_2 it is 0. Hydrogen undergoes neither oxidation nor reduction. Hence oxygen undergoes both oxidation to O_2 and reduction to H_2O. H_2O_2 is thus both an oxidising and a reducing agent. Such a molecule is said to *auto-oxidise*.

The concept of oxidation numbers is useful in *balancing chemical reactions.* In balancing equations, we take into account mass and charge conservation. Balancing chemical equations becomes easy when we match the total number of atoms and the total oxidation number of each atom on either side of a chemical reaction.

Example 12.5 Balance the following chemical equation:
$$K_2Cr_2O_7 + H_2O + S \rightarrow SO_2 + KOH + Cr_2O_3$$
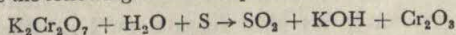
For this let us first assign the oxidation numbers:

$$K_2\ Cr_2\ O_7 + H_2\ O + S \rightarrow S\ O_2 + K\ O\ H + Cr_2\ O_3$$
$$+1\ +6\ -2\quad +1\ -2\qquad 0\quad +4\ -2\quad +1\ -2\ +1\quad +3\quad -2$$
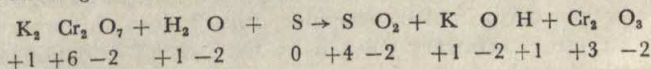
Chromium undergoes reduction from $+6$ state in $K_2Cr_2O_7$ to $+3$ state in Cr_2O_3. Sulphur gets oxidised from 0 in S to $+4$ in SO_2. Potassium, hydrogen and oxygen do not undergo any change. The reduction in the oxidation number of each chromium must come from that of sulphur. In order that the oxidation number balance (charge balance) be maintained, for every two $K_2Cr_2O_7$ molecules that disappear (that is a total reduction of 12 in the oxidation number of four Cr atoms, -3 for each atom), three sulphur atoms must be used up ($3 \times +4 = 12$). Hence we write:

$$2K_2Cr_2O_7 + H_2O + 3S \rightarrow 3SO_2 + 4KOH + 2Cr_2O_3$$
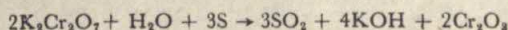
We have achieved charge balance. We should now do a mass (or atom) balance. Accounting for potassium atom balance gives us 4KOH on the right, which also balances O and H.

$$2K_2Cr_2O_7 + 2H_2O + 3S \rightarrow 3SO_2 + 4KOH + 2Cr_2O_3$$
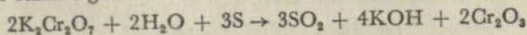
This equation is balanced both in mass and in ('formal') charge, and denotes the oxidation of S to SO_2 by $K_2Cr_2O_7$ which gets reduced to Cr_2O_3.

Example 12.6 Balance the equation: $KClO_3 \rightarrow KCl + O_2$.

Let us denote the oxidation numbers, and do the oxidation number balance first:

$$\begin{array}{ccccccc} K & Cl & O_3 & \rightarrow & K & Cl & + & O_2 \\ +1 & +5 & -2 & \rightarrow & +1 & -1 & & 0 \end{array}$$
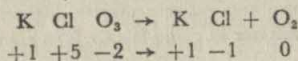
Chlorine gets reduced by 6 units and oxygen increases its oxidation number by 2. For oxidation number balance, we need six oxygen atoms for every chlorine atom, since potassium is unchanged.

$$KClO_3 \rightarrow KCl + 3O_2$$
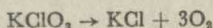
Let us now balance the oxygen atoms. There are six on the right but three on the left. Multiply the left-hand side by two.

$$2KClO_3 \rightarrow KCl + 3O_2$$
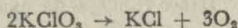
Now balance the K and Cl atoms on both sides:

$$2KClO_3 \rightarrow 2KCl + 3O_2$$
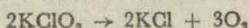
This is the balanced equation showing a reduction of chlorine and oxidation of oxygen upon decomposition of $KClO_3$.

Example 12.7 Write the balanced equation for the production of Cl_2 from aqueous HCl and MnO_2.

Let us first write the basic or skeletal equation:

$$\begin{array}{ccccccc} Mn & O_2 & + & Cl^- & \rightarrow & Cl_2 & + & Mn^{2+} \\ +4 & -2 & & -1 & & 0 & & +2 \end{array}$$
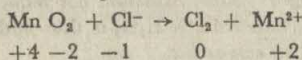
Balancing the total oxidation numbers, charges and atoms, and remembering that the reaction is in acid medium:

$$4H_3O^+ + MnO_2 + 2Cl^- \rightarrow Mn^{2+} + Cl_2 + 6H_2O$$
$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$
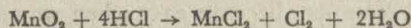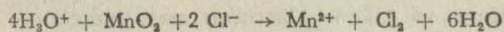
12.3.2 Balancing Equations Using Half-reactions

In section 12.2.1, we introduced the idea of half-reactions. Combination of an oxidation half-reaction with a reduction half-reaction yields a complete reaction, and charge balance is maintained in the process. This offers an alternate way of balancing chemical reactions. The use of half-reactions and the definition of redox reactions as involving electron transfer have the advantage of being more realistic as these occur in electrochemical cells. Besides, this procedure does not involve the use of arbitrary rules, as in the case of oxidation numbers. But either method can be used, whichever is rapid and less difficult. Let us now use the idea of half-reactions in balancing the reaction given in the example below.

Example 12.8 The half-reaction involving the reduction of Mn is

$$MnO_2 + 2e^- \rightarrow Mn^{2+}$$
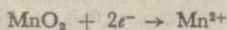
Charge balance and the fact that the reaction occurs in acid medium require,

$$MnO_2 + 2e^- + 4H_3O^+ \rightarrow Mn^{2+} + 6H_2O$$
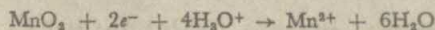
The oxidation half-reaction is

$$Cl^- \rightarrow \tfrac{1}{2} Cl_2 + e^-$$

The redox reaction is

$$MnO_2 + 4H_3O^+ + 2Cl^- \rightarrow Mn^{2+} + 6H_2O + Cl_2$$
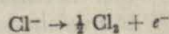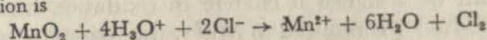
We note here that balancing of reactions by the oxidation number method and by using half-reactions yield identical results. Further, matching the sum of the oxidation numbers on either side of a chemical equation, as done in the oxidation number method, is equivalent to matching the number of electrons on either side. One can therefore employ either method for balancing equations. Balancing thus involves, (i) writing the skeletal half-reactions, (ii) balancing with respect to atoms, (iii) balancing charges, and (iv) adding the half-reactions to give the final equation. If a reaction is specified to be in acid medium, balancing is achieved by adding H_3O^+ to get the atom balance. Likewise, H_2O and OH^- are added to balance equations in basic media. Let us look at another example.

Example 12.9 Balance the following equation occurring in basic medium:

$$MnO^-_4 + SO^{-2}_3 \rightarrow MnO_2 + SO^{2-}_4$$
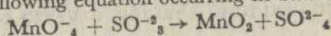
The half-reaction
$$\begin{array}{ccc} MnO^{3-}_4 \rightarrow & Mn & O_2 \\ +7\ -2 & +4 & -2 \end{array}$$

involves a decrease in the oxidation number of manganese by 3. Hence manganese gets reduced in this reaction. For charge balance, three electrons are added on the left-hand side. Atom balance requires addition of OH^- (basic solution) and water:

$$2H_2O + MnO^-_4 + 3e^- \rightarrow MnO_2 + 4OH^-$$

The other half-reaction
$$\begin{array}{ccc} S\ O^{2-}_3 & \rightarrow & S\ O^{2-}_4 \\ +4\ \ -2 & & +6\ -2 \end{array}$$
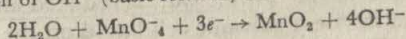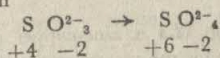
involves an oxidation of sulphur, by an increase in its oxidation number by 2. Let us thus add $2e^-$ on the right-hand side. Atom balance (in basic solution) needs OH and H_2O:

$$SO^{2-}_3 + 2\ OH^- \rightarrow SO^{2-}_4 + 2e^- + H_2O$$
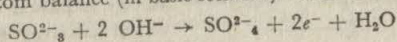
Let us add the two-half reactions:

$$MnO^-_4 + 3e^- + 2H_2O \rightarrow MnO_2 + 4\ OH^-$$
$$SO^{2-}_3 + 2\ OH^- \rightarrow SO^{2-}_4 + 2e^- + H_2O$$
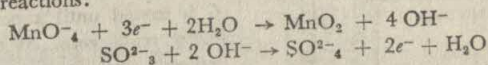
For total charge and atom balance, we need to multiply the first equation above by two and the second by three and add:

$$2MnO^-_4 + 6e^- + 4H_2O \rightarrow 2\ MnO_2 + 8\ OH^-$$
$$3SO^{2-}_3 + 6\ OH^- \rightarrow 3SO^{2-}_4 + 6e^- + 3H_2O$$

$$\overline{2MnO^-_4 + 3SO^{2-}_3 + 4H_2O + 6OH^- \rightarrow 2MnO_2 + 3SO^{2-}_4 + 8OH^- + 3H_2O}$$
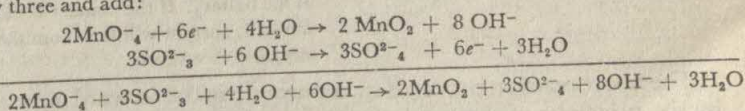
Simplifying this (by cancelling extra molecules of water and OH^- ions) we get the final balanced redox reaction:

$$2MnO^-_4 + 3SO^{2-}_3 + H_2O \rightarrow 2MnO_2 + 3SO^{2-}_4 + 2OH^-$$
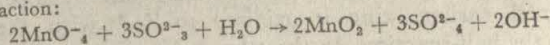
12.3.3 Redox Titrations

Redox titrations can be performed in the same manner as acid-base titrations (Chapter 11) by titrating one reagent with the other. The end point is detected with the help of a redox indicator which changes colour on oxidation or reduction. In some cases, such as oxidation by permangnate ions, the reactant itself undergoes colour change and functions as an indicator. For stoichiometric

calculations, one can employ either normality (and the relation $N_1V_1 = N_2V_2$) or molarity of solutions. Equivalent mass of a solute taking part in a redox reaction can be assigned if change in oxidation number is known. For example, when MnO^-_4 is reduced to Mn^{2+}, the oxidation number changes by 5 (from $+7$ to $+2$). The equivalent mass of MnO^-_4 is thus $\frac{1}{5}$ of the molecular mass since five mole of electrons are needed. Similarly when MnO_4 is reduced to MnO_2, the equivalent mass is $\frac{1}{3}$ of the molecular mass.

12.4 GALVANIC CELLS

After this digression into the utility of half-cell reactions in balancing equations, let us get back to the electrode processes. We noted that electrical energy is absorbed in an electrolytic cell producing a chemical reaction. This process can also be reversed, in which case chemical energy will have been converted to electrical energy. This possibility seems to have been recognised as early as 250 B.C., since it is suspected that the Parthians employed electrical cells. The modern electrochemical cell, called a *galvanic cell*, is derived from the devices pioneered by Luigi Galvani and Alessandro Volta of Italy about 200 years ago.

12.4.1 Working of a Galvanic Cell

If a zinc rod is dipped in a solution of copper sulphate, the following reaction occurs:

$$Zn(s) + CuSO_4(aq) \rightleftharpoons ZnSO_4(aq) + Cu(s)$$
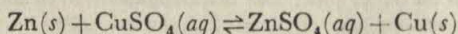
Metallic zinc is oxidised to Zn^{2+}, while Cu^{2+} is reduced and is deposited as solid copper metal. We can devise a galvanic cell based on the above reaction. Such a cell is illustrated in Fig. 12.3.
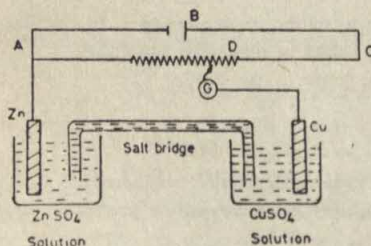
Fig. 12.3 A zinc-copper galvanic cell, with a set up for the measurement of its voltage by a potentiometer circuit. Current from battery B of known voltage is passed through the potentiometer wire AC of uniform resistance, thus calibrating the wire. The contact on AC from the galvanometer G is moved until a point D when the galvanometer reads zero. At this part, the emf of the galvanic cell is given by $(AD/AC) \times B$ where AD and AC are the wire lengths and B the voltage of the battery. If the contact is moved from D towards A, current will flow from the cell to the battery, and vice versa.

The above reaction proceeds spontaneously in the forward direction, governed by the principles of chemical equilibrium (enunciated in Chapter 10); the free energy released in the forward reaction would normally appear as heat energy. As mentioned earlier, zinc is oxidised to Zn^{2+} with the release of two electrons in the half-reaction. In the other half-reaction, Cu^{2+} ion picks up two electrons and get reduced to copper. By carrying out the two half-reactions in two different compartments, and allowing the electrons to flow through an external circuit as shown in Fig. 12.3, it is possible to convert at least a part of the free energy into useful electrical energy. In the galvanic cell shown, the metal wire of the external circuit and the *salt bridge* complete the electrical circuit and permit the flow of electrons from zinc to copper.

The salt bridge consists of a U-tube filled with an aqueous solution of an electrolyte such as KCl kept in a gel, so that conduction occurs but no direct mixing of the reactants.

The zinc compartment where oxidation occurs is the anode, and the copper compartment where reduction occurs is the cathode.

Under appropriate conditions, i.e. when $[ZnSO_4] = [CuSO_4] = 1\ M$, and $25°C$, the zinc-copper galvanic cell yields an *electromotive force* (emf) of $1.107V$. Such a galvanic cell is generally written in the following notation:

$$Zn \mid Zn^{2+}\ (1M) \parallel Cu^{2+}\ (1M) \mid Cu$$
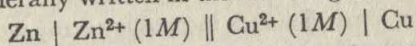
Here the anode (zinc in contact with $1M\ Zn^{2+}$ ions) is written to the left of the double vertical lines, and the cathode to the right. The single vertical lines represent the separation of the solid phase and the electrolyte solution. The double vertical line represents the separation of the two-half-cells. The anode reaction is,

$$Zn(s) \rightarrow Zn^{2+}\ (aq) + 2e^-$$
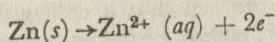
and the cathode reduction is,

$$Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$$
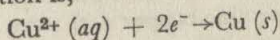
In general, we may represent a galvanic cell as

$$A \mid A^{n+}(xM) \parallel B^{n+}(y\ M) \mid B$$

where the reactions are:

ANODE: $A \rightleftharpoons A^{n+} + ne^-$

CATHODE: $B^{n+} + ne^- \rightleftharpoons B$

OVERALL: $A + B^{n+} \rightleftharpoons A^{n+} + B$
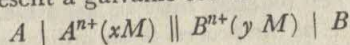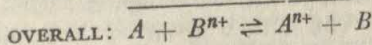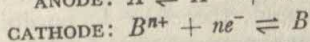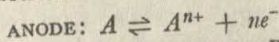
The liberated free energy appears (at least partly) as electrical energy. When such a galvanic cell is set up, electrons will flow in the direction determined by the relative ' potential ' of one electrode with respect to the other. When the two electrodes acquire the same potential, the free energy difference is zero, and there will be no passage of current. The galvanic cell is drained and the system is then in dynamic equilibrium.

12.4.2 Thermodynamics of Galvanic Cells

The emf that a galvanic cell yields can be used to perform work. This is referred to as *electrochemical energy conversion* and is quite similar to other forms of energy conversion that we know of, such as in a steam engine (where volume expansion is used to produce work) or in an internal combustion engine (where chemical energy is the primary source). In a galvanic cell, chemical reactions yield electrical energy. We have seen earlier that oxidation (or reduction) of an equivalent mass of a substance in a cell involves one Faraday of charge (96,487 coulombs). The total electrical work involved in the cell is given by the product of the charge and the voltage of the cell (work done to move a charge across a potential difference). This may be expressed as:

$$ELECTRICAL\ WORK = nFE$$

where n is the number of electrons involved in the redox reaction of the cell. The unit of electrical work is given by volt coulombs or Joules. To convert this to the familiar calories, the conversion factor of 4.184 is used; 1 Joule is equal to 4.184 calories or a faraday is equal to 23.07 kcal volt^{-1}. For examp'e,

the electrical work available from a zinc/copper galvanic cell of emf 1·107 V
is given by

$$\text{WORK} = 2 \times 96,487 \times 1\cdot1 \text{ Joules} = 2 \times 23\cdot07 \times 1\cdot1 \text{ kcal} = 50\cdot8 \text{ kcal}$$

The value of $n=2$ is used here since the electrode reactions involve the transfer
of two electrons.

A cell that yields a positive emf will be able to perform work while that with
a negative emf ($E<0$) will consume work or energy. A cell with redox reaction
that yields no net emf ($E=0$) is incapable of any work. Thus, the relation bet-
ween E and the chemical free energy is obvious. A process with a net negative
free energy ($\Delta G<0$) will be capable of performing useful work. We may
therefore write:

$$\Delta G = -nFE$$

The negative sign emphasises the fact that a cell with net *negative free energy*
change will produce *positive emf* that çan be harnessed to do work. One with net
positive free cnergy difference will consume work.

The chemical reactions in the zinc-copper cell were given earlier in section
12.4.1. From our foregoing arguments we see that since the cell yields a positive
emf, the ΔG for the cell reaction must be negative. Two points are of interest
here: (i) The ΔG or E of the process is an indication of the maximum amount
of work that is realisable in the system. (It should be noted that the symbol E
in this chapter stands for emf and *not* energy.) (ii) The total cell is a combi-
nation of two electrode reactions. It should, therefore, be possible to assign
emf values for each half-cell reaction, just as we assign ΔG values for these
individual reactions. The total cell emf is then given by the addition of the
oxidation potential (emf of the oxidation reaction) of the oxidised species and the
reduction potential of the reduced species. In other words, the *total emf* of the
galvanic cell is equal to *oxidation potential of the oxidised species plus reduction
potential of the reduced species,* just as the total ΔG of the cell reaction is equal
to ΔG of oxidation of the oxidised species plus ΔG of reduction of the reduced
species. It follows then that if the emfs of the oxidation and reduction reactions
add up to a value greater than zero (i.e. total $\Delta G<0$) the cell can do work.

Since any electrode reaction can be written as an equilibrium process (e.g.
$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$), the oxidation potential and the reduction potential
for this half-cell reaction are equal in value but opposite in sign. The total
cell emf may thus be expressed as

$$E_{\text{total}} = (E_{\text{ox}_A} + E_{\text{red}_B}) \text{ or } - (E_{\text{red}_A} - E_{\text{red}_B})$$

Here, the subscripts 'ox' and 'red' refer to oxidation and reduction, and A and B
refer to the two electrode reactions. For example, the reduction potential of
zinc is $-0\cdot764$ V and the reduction potential of copper is $0\cdot337$ V. The total
cell emf of this galvanic cell, depicted in Fig. 12.3 is $0\cdot764+0\cdot337=1\cdot101$ V
at 25°C, and the reaction occurring in the zinc/copper cell will be the oxida-
tion of zinc and reduction of Cu^{2+} to copper. One may also visualise this as
follows. Since the oxidation potential of zinc is $+0\cdot764$ V, oxidation of zinc is
a spontaneous process; likewise, reduction of Cu^{2+} is spontaneous in the other
half-cell.

12.4.3 Standard Half-cell Potentials

If the half-cell potentials, i.e. the emf values of electrode reactions, are known or calculable then it would be possible to calculate the emf of any galvanic cell. It would be given simply by the addition of the half-cell oxidation potential of the oxidised species and the half-cell reduction potential of the reduced species. Unfortunately, there is no way of isolating a single electrode reaction and it is therefore impossible to directly determine half-cell potentials. However, if we choose a given electrode as an arbitrary standard or reference, we may assign electrode potentials for other electrode processes with respect to the reference electrode. It has been universally accepted to assign to the hydrogen electrode with the half-cell reaction,

$$\tfrac{1}{2}H_2 \text{ (1 atm) } (g) \rightleftharpoons H^+ (aq) + e^-$$
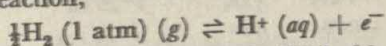
an electrode potential of 0·000 V at 25°C. With this reference electrode, the electrode potentials of many others are easily obtained. For example, if we want to obtain the potential of the copper electrode reaction, we design a galvanic cell comprising the hydrogen electrode as anode and the copper electrode as the cathode.

$$\begin{array}{c|c||c|c} H_2 (g) & H_3O^+ (aq) & Cu^{2+} (aq) & Cu (s) \\ (1 \text{ atm}) & 1 M & 1 M & \end{array}$$

The half-cell reactions are:
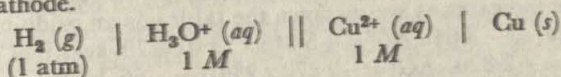
$$\tfrac{1}{2} H_2 (g) \text{ (1 atm) } \rightleftharpoons H^+ (aq) + e^-$$
$$Cu (s) \rightleftharpoons Cu^{2+} (aq) + 2 e^-$$
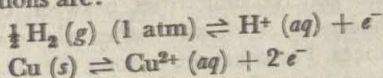
The first reaction, being at the anode, is an oxidation reaction, i.e. proceeds from left to right. The second reaction will then be a reduction reaction at the cathode, i.e. proceeds from right to left. The total emf of the galvanic cell will be the contribution from the two half-cell potentials, and can be measured by using a potentiometer as depicted in Fig. 12.3. The measured emf will give us the electrode potential of the copper electrode directly, since the hydrogen electrode potential is defined as 0·000 V.

Table 12.1 lists the standard reduction potentials of several electrode reactions. This means that when the reaction is written in the form

$$\text{OXIDANT} + n e^- \rightleftharpoons \text{REDUCTANT}$$
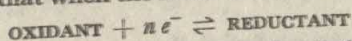
the emf listed is for the reduction reaction, that is for the reaction proceeding from left to right. The oxidation potential is the emf for the reverse reaction proceeding from right to left. The oxidation potential and the emf for the reverse reaction, have the same value but opposite sign as that of the reduction potential. All the half-cell potentials are represented by E°. The superscript zero specifies that the value is under standard conditions, where the concentrations of the various species involved are unity, i.e. species in solution are of unit molarity and gases are at 1 atmospheric pressure. The corresponding free energy change of the reaction $\Delta G^\circ = -nFE^\circ$ is also a standard state value.

The numerical value of the reduction potential of a reaction determines the tendency of the reaction to proceed from left to right. Any reaction with a large reduction potential has a great tendency to proceed towards right. It will be easier to reduce Ag^+ to silver ($E^\circ_{Ag} = 0·80$ V) than to reduce Zn^{2+} to zinc ($E^\circ_{Zn} = 0·76$) or we may say that zinc is a better reducing agent compared to silver. This becomes more obvious if we compute the free energy changes corresponding to the standard reduction potentials. The standard free energy ΔG° corresponding to E°_{Ag} is more negative than that of E°_{Zn}. Thus it is easier to

Table 12.1 Standard Reduction Potentials at 25°C

Half-reaction	$E°$ (V)	Half-reaction	$E°$ (V)
$Li^+ + e^- \rightleftharpoons Li$	$-3\cdot045$	$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2$	$+0\cdot000$
$K^+ + e^- \rightleftharpoons K$	$-2\cdot924$	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	$+0\cdot154$
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	$-2\cdot866$	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	$+0\cdot337$
$Na^+ + e^- \rightleftharpoons Na$	$-2\cdot714$	$Cu^+ + e^- \rightleftharpoons Cu$	$+0\cdot521$
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	$-2\cdot360$	$\frac{1}{2} I_2 + e^- \rightleftharpoons I^-$	$+0\cdot537$
$Al^{3+} + 3e^- \rightleftharpoons Al$	$-1\cdot660$	$\frac{1}{2} Br_2 + e^- \rightleftharpoons Br^-$	$+1\cdot065$
$SiF_6^{2-} + 4e^- \rightleftharpoons Si+6F^-$	$-1\cdot240$	$\frac{1}{2} Cl_2 + e^- \rightleftharpoons Cl^-$	$+1\cdot358$
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	$-0\cdot764$	$Au^{3+} + 3e^- \rightleftharpoons Au$	$+1\cdot500$
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	$-0\cdot126$	$\frac{1}{2}F_2 + e^- \rightleftharpoons F^-$	$+2\cdot870$

reduce Ag^+ than Zn^{2+}, or zinc is a better reducing agent. Conversely, we may also say from Table 12.1 that the oxidising power of the species on the left-hand side increases as we go down the table. As an oxidising agent, Li^+ is the poorest $(E°=-3\cdot045, \Delta G°=+3\cdot045 \times 23\cdot07 = 70$ kcal mol$^{-1})$ while F_2 is the best $(E°=+2\cdot870, \Delta G°=-2\cdot870 \times 23\cdot07 = -66$ kcal$)$.

One might notice some general similarities between the series in Table 12.1, the so called *electrochemical series*, and other electronic and structural properties of these substances. For example, among the alkali metals, Li is the best reducing agent and the strength decreases as we go down the group. A similar trend is seen in the half-cell potentials. This stands to reason since the ionisation potentials of the alkali metals are roughly comparable but the hydration energy of Li^+ ion is the highest $(-121$ kcal mol$^{-1})$. Li^+ ion will be energetically the most stable ion in water, making Li^+ the poorest oxidising agent. On the same basis F_2 will be the best oxidiser (or F^- the best reducing agent) since the ionisation energy of F is much higher (408 kcal mol$^{-1})$ compared to that of Li (124·3), even though their hydration energies are comparable.

12.4.4 Computation of the emf of Cells

Let us now look at how galvanic cells can be constructed and the emf of such cells computed, from half-cell reactions. In a galvanic cell, the reaction that occurs is a redox reaction between two species A and B. The total cell standard emf is given by the sum of the standard oxidation potential of species A and the standard reduction potential of species B. The following example illustrates this point.

Example 12.10 Design an electrochemical cell that utilises the reaction:

$$Mg(s) + Cu^{+2}(aq) = Mg^{2+} (aq) + Cu(s)$$
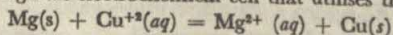
The half-cell potentials for the reactions are:

$$Mg^{2+} (aq) + 2e^- \rightleftharpoons Mg(s) \qquad E°_{red} = -2\cdot360 \text{ V}$$
$$Cu^{2+} (aq) + 2e^- \rightleftharpoons Cu(s) \qquad E°_{red} = 0\cdot337 \text{ V}$$
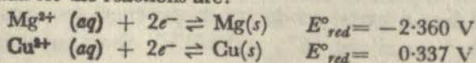
From the values, it is clear that Mg is a better oxidising agent, and Cu a better reducing agent. Since oxidation occurs at the anode and reduction at the cathode, Mg is the anode and Cu the cathode. We calculate the cell emf by adding the oxidation potential of Mg and the reduction potential of Cu. Thus, in the above example $E°_{cell} = 0\cdot337 + 2\cdot360 = 2\cdot697$ V.

The cell reaction can also be determined by subtracting the two reduction reactions. In order to avoid confusion, and to conform to the current conventions, the following rules will be helpful in computing the emf values of galvanic cells.

(1) Write the standard reduction potential for each half-cell.
(2) Subtract the reduction potential of the left electrode from that of the right electrode to obtain the total cell emf, $E°_{cell} = E°_{red}(right) - E°_{red}(left)$. [Note that this is the same as $E°_{ox}(left) + E°_{red}(right)$].
(3) If the cell emf turns out to be positive, the left electrode will be considered as the anode and the emf shall be the difference between the reduction reactions occurring at the right electrode and at the left electrode.
(4) If the cell emf is negative, the electrodes can be interchanged so that the total reaction is determined by rule 3.

In a galvanic cell, electrons are released at the anode by the oxidation occurring there. These electrons are sent to the external circuit by the anode. The anode is thus regarded as the negative electrode. The cathode is the electron sink (reduction occurs here) and thus the cathode is the positive electrode. In an electrolysis cell, electrons are fed into the cell from the external circuit. The cathode is still the electron sink. But since it receives electrons from the external circuit, it is the negative electrode and anode the positive electrode. Here also, oxidation occurs at the anode and reduction at the cathode.

Example 12.11 Calculate the standard emf of the cell

$$Zn \,|\, Zn^{2+} (1\ M) \,\|\, Mg^{2+}(1\ M) \,|\, Mg$$
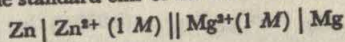
The reduction potentials for the zinc and the magnesium electrodes are, respectively, -0.764 and -2.360 V. Hence magnesium must be the reducing agent and zinc the oxidising. The cell reaction therefore, will be

$$Mg + Zn^{2+}(aq)\ (1\ M) \rightleftharpoons Zn + Mg^{2+}\ (aq)$$
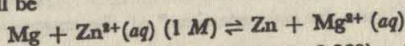
The cell emf is then, $E°_{red}(Zn) - E°_{red}(Mg) = -0.764 - (-2.360) = +1.596$ V

12.4.5 Concentration Dependence of emf: The Nernst Equation

The electrode potentials listed in Table 12.1 are for 1 molar solutions of the species involved, and for the equilibrium between oxidant and reductant. The corresponding standard state free energy change $\Delta G°$ for the electrode process is given by $\Delta G° = -nFE°$. What will happen to the value of the emf if the species are not at unit concentrations?

Since the half-reactions are written as equilibrium processes, the extent to which equilibrium is established will depend on the concentrations of the species involved; this is governed by the law of mass action and Le Chatelier's principle. The dependence of the free energy change ΔG, on the concentrations of species was discussed in Chapter 10. Let the general reaction given below form the basis of a galvanic cell:

$$aA + bB \rightleftharpoons cC + dD$$
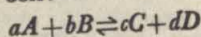
The free energy ΔG is given by,

$$\Delta G = \Delta G° + RT\ \ln \left[\frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \right]$$

where ΔG° is the free energy change for standard state, i.e. when the species are all of 1 M concentration. At equilibrium $\Delta G=0$, and the 'reaction quotient' given within the square brackets in the above equation become equal to the equilibrium constant. Since the emf of a cell and the free energy change are related, we may rewrite this equation as

$$E=E^\circ-\frac{RT}{nF}\ln\left[\frac{[C]^c[D]^d}{[A]^a[B]^b}\right]$$

Substituting for the values of R and F, and taking the temperature to be 25°C 298 K the above equation reduces to,

$$E=E^\circ-\frac{0.059}{n}\log\left[\frac{[C]^c[D]^d}{[A]^a[B]^b}\right]$$

This equation relates the emf of a galvanic cell and the concentrations of the species involved. It is valid for the complete cell as well as for half-cell reactions, and goes by the name *Nernst equation* (after Nernst who formulated it). The use of the Nernst equation in electrochemical cells is illustrated in Example 12.12 below.

Example 12.12 In Example 12.10, write the half-cell and total-cell potentials as a function of the concentrations of the species. Calculate the values of the potentials when $[Mg^{2+}]=0.001$ M and $[Cu^{2+}]=0.0001$ M. Assume $T=25$°C.
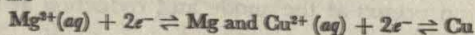
The half-cell reaction are
$$Mg^{2+}(aq)+2e^-\rightleftharpoons Mg \text{ and } Cu^{2+}(aq)+2e^-\rightleftharpoons Cu$$
In Example 12.10, half-cell reduction potentials are

$$E_{Mg^{2+}/Mg}=E^\circ_{Mg^{2+}/Mg}-(0.059/2)\log\frac{1}{[Mg^{2+}]}$$

and

$$E_{Cu^{2+}/Cu}=E^\circ_{Cu^{2+}/Cu}-(0.059/2)\log\frac{1}{[Cu^{2+}]}$$

where $[Mg^{2+}]$ and $[Cu^{2+}]$ are the concentrations* of the magnesium and copper ions. For the overall reaction

$$Mg(s)+Cu^{2+}(aq)=Mg^{2+}(aq)+Cu(s)$$
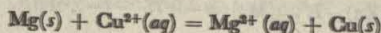
The cell potential is

$$E=E_{Cu^{2+}/Cu}-E_{Mg^{2+}/Mg}=E^\circ_{Cu^{2+}/Cu}-E^\circ_{Mg^{2+}/Mg}-\frac{0.059}{2}\log\frac{Mg^{2+}}{Cu^{2+}}$$

$$=E^\circ-\frac{0.059}{2}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

Thus we have,

$$E_{Mg^{2+}/Mg}=-2.36-\frac{0.059}{2}\log\frac{1}{0.001}$$

$$=-2.36+\frac{0.059}{2}\times3=-2.27\text{ V}$$

$$E_{Cu^{2+}/Cu}=0.34-\frac{0.059}{2}\log\frac{1}{0.0001}$$

$$=0.34+\frac{0.059}{2}\times4=0.46\text{ V}$$

Total cell potential$=0.46-(-2.27)=2.73$ V

*Concentrations of pure solids are taken equal to unity.

Alternatively,

$$E = E^\circ - \frac{0 \cdot 059}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$= 2 \cdot 70 - \frac{0 \cdot 059}{2} \log \frac{0 \cdot 001}{0 \cdot 001}$$

$$= 2 \cdot 70 + \frac{0 \cdot 059}{2} \log 10 = 2 \cdot 70 + 0 \cdot 03 = 2 \cdot 73 \text{ V}$$

Example 12.13 In a cell one electrode is made of silver metal immersed in 0·01 mol solution of silver nitrate. The second electrode is made of platinum over which hydrogen gas at 1 atmospheric pressure is bubbled and is dipped in a solution of unknown pH. What is the pH of solution if the cell potential is 1·04 V?

The cell reaction can be written as

$$H_2(g) + 2Ag^+ (aq) \rightleftharpoons 2H^+ (aq) + Ag(s)$$
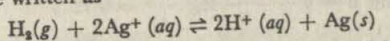
$$E_{H^+/\frac{1}{2}H_2} = E^\circ_{H^+/\frac{1}{2}H_2} - 0 \cdot 059 \log \frac{[H_2]}{[H^+]}$$

E for one atm hydrogen pressure $= 0 - 0 \cdot 059 \log \frac{1}{H^+} = -0 \cdot 059 \, p$H

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} - 0 \cdot 059 \log \frac{1}{[Ag^+]}$$

$$= 0 \cdot 80 - 0 \cdot 059 \log \frac{1}{0 \cdot 01} = 0 \cdot 80 + 0 \cdot 059 \times 2 = 0 \cdot 92 \text{ V}$$

Cell potential $= 1 \cdot 04 = 0 \cdot 92 + (0 \cdot 059 \, pH)$. Hence pH $= 2 \cdot 00$.

The galvanic cell described in Example 12.13 forms the basis of a method for measuring the pH of aqueous solutions. A hydrogen electrode (or an equivalent one that is sensitive to H_3O^+) is coupled with a standard electrode and the cell emf measured. From the emf value, the pH of the solution is determined.

12.4.6 Concentration Cells
The Nernst equation suggests that we should be able to obtain electrical energy by a concentration difference alone, without any chemical reactions; because, E° being the same for both electrodes, E will depend on the concentration. For example consider the following cell,

$$Cu \mid CuSO_4 (x \, M) \; \vdots \; CuSO_4 (y \, M) \mid Cu$$

The half-reactions are

LEFT: $Cu(s) \rightleftharpoons Cu^{2+} (x \, M) + 2e^-$

RIGHT: $Cu^{2+} (y \, M) + 2e^- \rightarrow Cu(s)$

OVERALL: $Cu^{2+} (y \, M) \rightarrow Cu^{2+} (x \, M)$
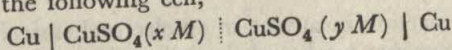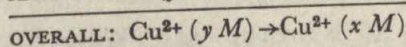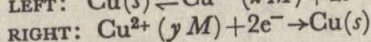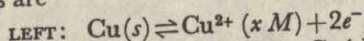
The cell potential: $E = 0 - (RT/nF) \ln x/y$
or $E = (RT/nF) \ln y/x$

The cell emf is positive if $y > x$, and implies a transfer of material from a more concentrated to a dilute solution. This as we know, is a spontaneous process occurring by *diffusion*.

From the above discussion it follows that if we were to set up a galvanic cell with the two electrodes differing from each another only in the concentration

of the solutions, a cell emf will be developed arising only due to the concentration difference. The corresponding free energy change will be a measure of the diffusion of the electrolyte. Such cells based on concentration differences between the two electrodes are termed *concentration cells*. The cell emf of a concentration cell simply measures the tendency of the spontaneous process of diffusion.

Example 12.14 Calculate the emf at 25°C, of the concentration cell

$$Ag \mid AgNO_3(0 \cdot 01 \ M) \mid AgNO_3(1 \ M) \mid Ag$$
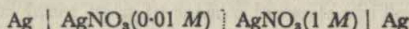
The net cell reaction is

$$Ag^+ (1 \ M) \rightarrow Ag^+ (0 \cdot 01 \ M)$$

$$\text{and } E = 0 - \frac{0 \cdot 059}{1} \log \frac{0 \cdot 01}{1} = 0 \cdot 12 \text{ V}$$

We have encountered the term solubility product, K_{sp}, in Chapter 11. Example 12.15 shows how the solubility product of a sparingly soluble salt can be measured by setting up a concentration cell.

Example 12.15 In order to determine the solubility product of AgCl in water, the half-cell Ag/AgCl was connected to a half-cell consisting of a silver wire immersed in a solution of 1 M NaCl and some suspended AgCl. The emf of the cell so constructed is 0 556 V at 25°C. What is the K_{sp} of AgCl?

$$\text{The cell is: } Ag \mid AgCl \left| \begin{array}{c} 1 \ M \ \ Cl^- \\ (Ag^+ \ Cl^-) \end{array} \right| Ag$$
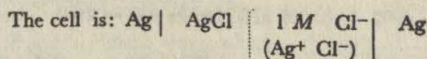
In the right half-cell $[Ag^+] = K_{sp}/[Cl^-] = K_{sp}/1$

$$\text{Hence } E = 0 - \frac{0 \cdot 059}{1} \log \frac{[Ag^+]_{\text{right}}}{[Ag^+]_{\text{left}}}$$

$$= 0 - 0 \cdot 059 \log \frac{K_{sp}/1}{1} = -0 \cdot 059 \log K_{sp}$$

$$E = 0 \cdot 556 \text{ V} = -0 \cdot 059 \log K_{sp}. \text{ Hence } K_{sp} = 2 \cdot 8 \times 10^{-10}$$

12.5 CELL emf AND EQUILIBRIUM CONSTANT

When the cell reaction occurring in an electrochemical cell is at equilibrium, the system does no net work and the cell emf is zero. Under these conditions the Nernst equation reduces to,

$$E° = \frac{RT}{nF} \ln K$$

The standard free energy $\Delta G°$ is given by $-nFE°$. We see that from a knowledge of $E°$ we can obtain information regarding the equilibrium constant, standard free energy change and the spontaneity of the cell reaction.

Example 12.16 Will magnesium reduce $CuSO_4$?

The standard reduction potential of Mg/Mg^{2+} and Cu/Cu^{2+} systems are $-2 \cdot 360$ and $0 \cdot 337$ V respectively. Hence for the reaction $Mg + Cu^{2+} \rightleftharpoons Mg^{2+} + Cu$ the standard cell emf, $E° = 2 \cdot 697$ V (see Example 12.10 for details).

$2.697 = \dfrac{0.59}{2} \log K$ at 25°C, hence $K = 10^{90}$.

Also $\Delta G° = -nFE° = -125$ kcal

The very high value of K and the large negative $\Delta G°$ both predict that Mg will reduce $CuSO_4$. The reduction will be highly spontaneous.

Example 12.17 The standard free energy change for the reaction

$$H_2(g) + 2AgCl(s) = 2Ag(s) + 2H^+(aq) + 2Cl^- (aq)$$
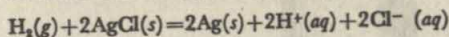
is -10.26 kcal mol^{-1} at 25°C. A cell, using the above reaction, is operated at 25°C, under the following conditions: pressure of $H_2(g) = 1$ atm, and molarities of H^+ and $Cl^- = 0.1$. Calculate the emf of the cell.

$$\Delta G° = -nFE° = -10.26 \text{ kcal}$$

$n = 2$ since the reaction above uses two moles of AgCl to react with H_2.

$$F = 96487 \text{ coulombs} = 23.07 \text{ kcal vol}^{-1}$$

Hence $E° = \dfrac{-10.26}{-(2 \times 23.07)} = 0.222$ V

This is of course the value of $E°$ that we would get from standard half-cell potential tables.*

$$E = E° - 0.059 \log \frac{[H^+]^2 [Cl^-]^2}{[H_2]}$$

$$= 0.222 - \frac{0.059}{2} \log \frac{(0.1)^2}{1}$$

$$= 0.222 + \frac{0.059}{2} \times 4 = 0.340 \text{ V}$$

12.6 COMMERCIAL APPLICATIONS OF GALVANIC CELLS

It is apparent from the above discussion that a proper choice of two half-cell reactions put together in a vessel ought to give us a convenient source of electrical energy. Practical considerations limit the choice of the two half-cells. Depending on the types of reactions that are involved, the emf also varies. We give below some examples of commercial cells.

12.6.1 The Dry Cell

This is also called *LeClanche cell* and is commonly used in flashlights, transistor radios and many other devices. This is shown schematically in Fig. 12.4. In this cell, zinc (the cylinder vessel material) acts as the anode and a graphite rod is the cathode. The graphite rod is surrounded by a paste of manganese

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*The standard potential for the reaction $AgCl + e^- \rightarrow Ag(s) + Cl^-$ is 0.222 V, is the same no matter how many moles of AgCl we take. This is because $E°$ is an intensive property like temperature or volume. But $\Delta G°$ is an extensive property that depends on the quantity or mass. We use the values of $n = 2$ to obtain $\Delta G°$. We could have written the cell reaction as $\frac{1}{2}H_2 + AgCl \rightarrow Ag + H^+_{0.1} + Cl^-_{0.1}$; with $n = 1$. Then

$$E = 0.222 - 0.059/1 \log (0.01)(0.1)/1$$
$$= 0.222 - 0.059 \log 10^{-3} = 0.34 \text{ V}$$

Since the amounts of the reactants are reduced by two, the $\Delta G°$ would be -5.13 kcal here.

POSITIVE

NEGATIVE

GRAPHITE ROD

PASTE OF MnO$_2$
ZnCl$_2$ AND AMMONI-
-UM CHLORIDE

ZINC VESSEL

PAPER FOR
INSULATION
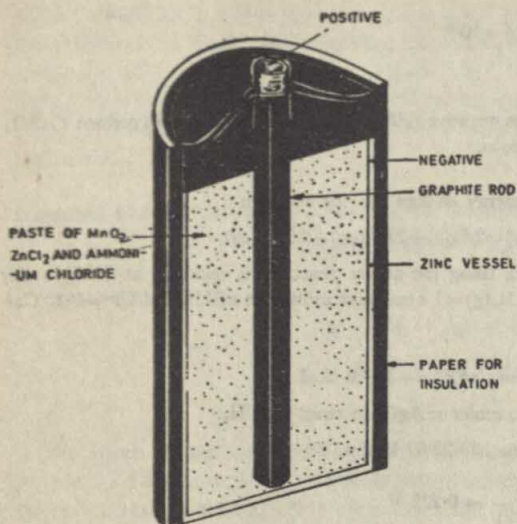
Fig. 12.4 Cross-sectional view of a dry cell

dioxide, zinc chloride and ammonium chloride. The following reactions take place at the electrodes.

$$Zn(s) \rightarrow Zn^+ + 2e^- \qquad \text{(ANODE)}$$

$$2\,NH^+_4 + 2MnO_2 + 2e^- \rightarrow Mn_2O_3 + 2NH_3(aq) + H_2O \qquad \text{(CATHODE)}$$
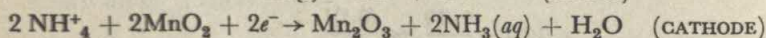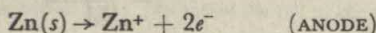
The cell is 'dry' only because it contains a paste and no liquid. The voltage of the commercially available dry cell is about 1·5 V, but compact batteries of high voltage are available with a number of such cells assembled in series.

12.6.2 Lead Storage Battery

This is commonly used in automobiles and is also known as the *lead accumulator*. The main advantage of this cell is that after it has been discharged due to usage, it can be charged again by reversing the reactions, by applying a current to the discharged cell. Fig. 12.5 shows the components of an accumulator.

It consists of electrodes of lead and lead dioxide dipped in a solution of dilute sulphuric acid. When the cell is under use the lead electrode acts as

Pb–Sb alloy
grid

PbO$_2$

Pb metal

Separator

Dil. H$_2$SO$_4$
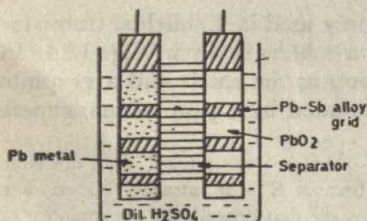
Fig. 12.5 A lead accumulator

an anode and the lead dioxide electrode acts as a cathode. The electrode reactions are:

ANODE: $Pb(s) + HSO^-_4 + H_2O \rightarrow PbSO_4(s) + 2e^- + H^+_3O\,(aq)$

CATHODE: $PbO_2(s) + HSO^-_4 + 3H_3O^+ + 2e^- \rightarrow PbSO_4(s) + 5H_2O$

The overall reaction is then

$$Pb(s) + 2HSO^-_4(aq) + 2H_2O^+(aq) + PbO_2(s) \rightarrow 2PbSO_4(s) + 4H_2O$$
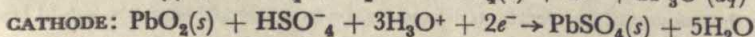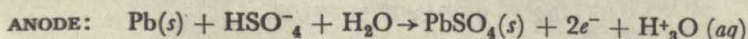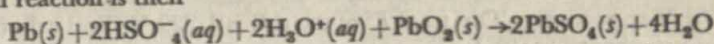
The lead sulphate formed in the reaction is insoluble and adheres to both the electrodes, and the concentration of sulphuric acid decreases. The battery can be charged by passing current in the opposite direction at a suitable voltage. The reactions at the electrodes are reversed and lead to the formation of Pb and PbO_2 and the replenishment of sulphuric acid.

12.6.3 Fuel Cells

In a conventional power plant for generating electricity, a chemical fuel is burnt and the liberated thermal energy is utilised to drive a turbine. The turbine is coupled to a generator and electricity is produced. The maximum efficiency of such a process is generally about 40 per cent. On the contrary, if the free energy of a chemical reaction can be directly converted to electricity by using a chemical reaction as the basis of a galvanic cell, the efficiency of such a *fuel cell* will be extremely high. There is considerable effort in recent years devoted to the construction of such fuel cells.
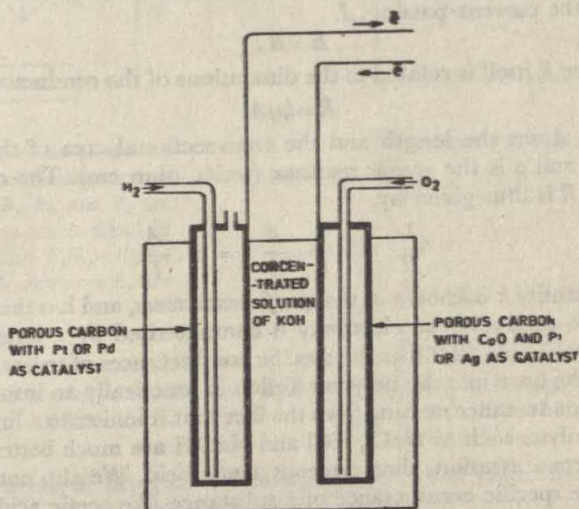
Fig. 12.6 Schematic diagram of a H_2-O_2 fuel cell

Fig. 12.6 shows a simple arrangement for a hydrogen-oxygen fuel cell. The electrodes are two porous vessels made by pressing carbon with suitable catalysts. In the anode vessel, the catalyst is finely divided platinum or palladium and in the cathode, a mixture of CoO and platinum or silver. The electrodes are dipped in a solution of potassium hydroxide, and hydrogen and oxygen are introduced at the anode and cathode respectively. The following reactions take place.

ANODE: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

CATHODE: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Overall reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
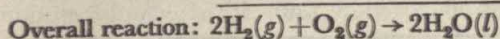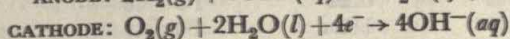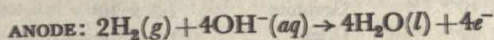
The standard emf value for the anode and cathode reactions are $+0.828$ and 0.401 V respectively. The total E^o of the cell is 1.229 V. Fuel cells of this kind produce about 2×10^5 Joules per mole of hydrogen spent, which means the efficiency of this cell is as high as 75 per cent.

12.7 CONDUCTION BY ELECTROLYTES

We shall now turn our attention to the conduction of electricity by electrolyte solutions. While the application of a direct current through a solution of an electrolyte results in redox reactions, the application of an alternating current (ac) leads to conduction only. Electrode reactions are prevented in an ac field since the electrodes change polarities very fast under the normal operating frequency. The electrode reaction occurring in the first half of the cycle is therefore reversed in the later half of the cycle. The conduction of current by electrolyte solutions can be studied quantitatively.

12.7.1 Conductance

Ohm's law relates the resistance offered by a medium, R, with the applied voltage, V and the current passing, I.

$$E = R I$$

The resistance R itself is related to the dimensions of the conductor as

$$R = l\rho/A$$

where l and A are the length and the cross-sectional area of the conductor respectively, and ρ is the *specific resistance* (units, ohm cm). The conductance, defined as $1/R$ is thus given by,

$$\frac{1}{R} = \frac{1}{\rho} \cdot \frac{A}{l} = k \cdot \frac{A}{l}$$

where the quantity k is known as the *specific conductance*, and has the units ohm^{-1} cm^{-1}. A good conductor of electricity is characterised by a large value of k and vice versa. Table 12.2 lists the specific conductances of several substances. Silver leads the list while the polymer Teflon is practically an insulator. Water shows some conductance, arising from the fact that it ionises to a limited extent. Strong electrolytes such as NaCl, HCl and NaOH are much better conductors at the same concentration, than aqueous acetic acid. We also notice from the table that the specific conductance of a substance like acetic acid varies with its concentration in solution. This stands to reason since k measures the conductance of 1 cm^3 of the solution and the conductance of an electrolyte depends on the number of the conducting species (ions) present in 1 cm^3, and therefore proportional to the concentration c in equivalents per litre.

Table 12.2 Specific Conductances of Some Substances

Substance	k (ohm^{-1} cm^{-1})	Substance	k (ohm^{-1} cm^{-1})
$0.1M$ HCl	3.5×10^{-2}	Silver metal	5.0×10^5
$0.1M$ NaCl	9.2×10^{-3}	Iron metal	1.0×10^5
$0.01M$ NaCl	1.2×10^{-3}	Graphite	1.2×10^2
$0.1M$ CH$_3$COOH	4.7×10^{-4}	Glass	1.0×10^{-14}
$0.01M$ CH$_3$COOH	1.6×10^{-4}	Teflon	1.0×10^{-18}
Water (very pure)	6.0×10^{-8}		

In order to compare quantitatively the conductivities of substances, it is convenient to employ a quantity called the *equivalent conductance*, Λ. It is related to the specific conductance by the relation,

$$\Lambda_c = 1000k/c$$

where Λ_c refers to the equivalent conductance of a solution whose concentration is c equivalent per litre. Thus, the equivalent conductance is the conductance of the solution containing one equivalent of the electrolyte and placed between two parallel electrodes 1 cm apart. It is advantageous to use Λ, since changes of Λ with concentration may be attributed directly to the number and the mobility of ions present in solution.
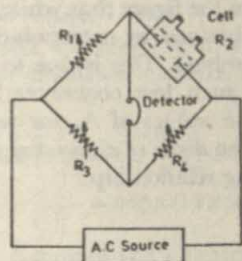
Fig. 12.7 Wheatstone bridge arrangement for measuring solution resistance. R_1, R_2, R_3, and R_4 are adjusted so as to get no signal in the detector, then $R_1/R_2 = R_3/R_4$. If R_1, R_3 and R_4 are known R_2 can be calculated.
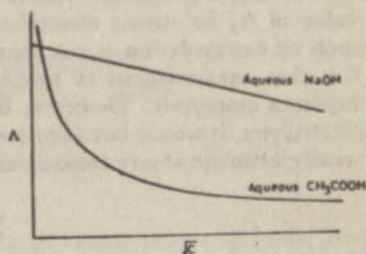
Fig. 12.8 Variation of Λ with c

Experimental determination of the conductance of a solution is achieved by means of a conductance cell and a Wheatstone bridge arrangement shown in Fig. 12.7.

12.7.2 Variation of Equivalent Conductance with Concentration

Fig. 12.8 shows how the equivalent conductances of a strong electrolyte and a weak electrolyte vary with concentrations. In the figure, Λ is plotted against $\sqrt{c}$ since it is more convenient to represent the concentration dependence in this manner. A *strong electrolyte* is one which exists in a completely ionised form at all concentrations of interest in solution, i.e. its *degree of dissociation* is infinity. We notice from Fig. 12.8 that the equivalent conductance of the strong electrolyte NaOH decreases only slightly with increasing concentration. This decrease is not due to a change in the number of ions with concentration. At high concentrations, attraction between Na^+ and OH^- increases due to the greater number of ions per unit volume. Besides there is always a viscous drag experienced by an ion due to solvation by the solvent molecules.

Some drag results from the motion of the oppositely charged ions moving in opposite directions. Ideal behaviour is thus to be expected only in the limit of infinite dilution. In this limit, both sodium and hydroxyl ions may be thought of as behaving essentially independent of each other. The *equivalent conductance*

at infinite dilution, Λ_0, may thus be thought of as the sum of the (infinite dilution) equivalent conductances λ^+_0 and λ^-_0 of the two ions.

The behaviour of a *weak electrolyte* such as acetic acid is quite different. By a weak electrolyte, we mean one that dissociates incompletely in solution, so that an equilibrium is set up between the undissociated molecule and the dissociated ions. This was exemplified earlier in Chapter 11. The dissociation constant in such cases is less than unity. As the concentration of the substance is decreased, more of it must ionise in accordance with the principles of equilibrium until at infinite dilution, the dissociation is complete (the degree of dissociation $\alpha=1$). The steep increase in equivalent conductance of the weak electrolyte CH_3COOH seen in Fig. 12.8, may thus be attributed essentially to an increase in the number of ions in solution. We also notice from the figure that while the value of Λ_0 for strong electrolytes can be easily obtained by extrapolation, such an extrapolation is not feasible for weak electrolytes. This is due to the fact that measurement of specific conductance at such low concentrations becomes inaccurate. However, if we did know the values of Λ_0 for weak electrolytes, it would becomes possible to calculate the *degree of dissociation* of a weak electrolyte at any concentration by the following relationship:

$$\alpha_c = \frac{\Lambda_c}{\Lambda_0}$$

Here, the subscript '*c*' refers to the concentration of the electrolyte in equivalent per litre.

12.7.3 Kohlrausch's Law

We have pointed out that at infinite dilution, the equivalent conductance of an electrolyte is essentially due to the ions that are unperturbed by any interionic or other influences. We may regard the conductance as due to contributions from the positive and negative ions:

$$\Lambda_0 = \lambda^+_0 + \lambda^-_0$$

This implies that the ionic conductance λ^+_0 of a cation (and likewise λ^-_0) is a quantity characteristic of a given ion regardless of what the counter ion is in the electrolyte. Kohlrausch concluded in 1875 after a study of the equivalent conductances of many electrolytes, that the total equivalent conductance at infinite dilution of an electrolyte is the sum of the equivalent conductances of the cation and the anion. The additive relation given above is referred to as *Kohlrausch's law* of independent migration of ions, and is useful for determining the Λ_0 values of weak electrolytes. As an example, let us compute the Λ_0 value of acetic acid employing Kohlrausch's law.

Example 12.18 What is the Λ_0 value of acetic acid, given the Λ_0 values of HCl, NaCl and CH_3COONa as 426·16, 126·45, and 91·01 ohm^{-1} cm^2 equivalent^{-1} respectively.

$$\Lambda_0 \ (CH_3COOH) = \lambda^+_0 \ (H^+) + \lambda^-_0 \ (CH_3COO^-) \quad (a)$$

$$\Lambda_0 \ (HCl) \quad\quad = \lambda^+_0 \ (H^+) + \lambda^-_0 \ (Cl^-) \quad\quad\quad (b)$$

$$\Lambda_0 \ (NaCl) \quad\quad = \lambda^+_0 \ (Na^+) + \lambda^-_0 \ (Cl^-) \quad\quad\quad (c)$$

$$\Lambda_0 \ (CH_3COONa) = \lambda^+_0 \ (Na^+) + \lambda^-_0 \ (CH_3COO^-) \quad (d)$$

Combining equations (*b*), (*c*) and (*d*) as (*b*) + (*d*) − (*c*), yields equation (*a*):

$$\Lambda_0\,(HCl) - \Lambda_0\,(NaCl) + \Lambda_0(CH_3COONa) = \lambda^+_0\,(H^+) + \lambda^-_0(Cl^-) - \lambda^+_0(Na^+) - \lambda^-_0(Cl^-)$$
$$+ \lambda^+_0\,(Na^+) + \lambda^-_0\,(CH_3COO^-)$$
$$= \lambda^+_0(H^+) + \lambda^-_0(CH_3COO^-) = \Lambda_0\,(CH_3COOH)$$

Hence $\Lambda_0(CH_3COOH) = \Lambda_0(HCl) - \Lambda_0(NaCl) + \Lambda_0(CH_3COONa)$
$$= 426 \cdot 16 - 126 \cdot 45 + 91 \cdot 01 = 390 \cdot 72$$

Example 12.19 The equivalent conductance at 25°C of a 0·05 *M* solution of acetic acid is 7·36. What is the dissociation constant of the acid?

We first calculate the degree of dissociation of acetic acid at 0·05 *M* concentration. Λ_0 is 390·72 and $\Lambda_{(0 \cdot 05)}$ is 7·36.

Hence, $a = 7 \cdot 36/390 \cdot 72 = 1 \cdot 9 \times 10^{-2}$

The dissociation equilibrium is: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$0 \cdot 05M\,(1-a) \qquad 0 \cdot 05a \qquad 0 \cdot 05a$$

Hence, $K = \dfrac{(0 \cdot 05)^2 a^2}{0 \cdot 05(1-a)} = 0 \cdot 05a^2$ (since $a < 1$)

$$= 0 \cdot 05 \times (1 \cdot 9 \times 10^{-2})^2 = 1 \cdot 8 \times 10^{-5}$$

Example 12.19 illustrates the use of conductance measurements in the determination of dissociation constants of weak electrolytes. From a measurement of the resistance of a solution of weak electrolyte of known concentration, the equivalent conductance can be computed. From a knowledge of Λ_0 of the electrolyte, the degree of dissociation and hence the value of *K* can be calculated.

Another use of conductance measurements is in estimating the solubility of sparingly soluble salts. The specific conductance of a solution of the sparingly soluble salt (or in fact even a suspension of the precipitate in water) is determined by experiment. Since the solubility of the salt is very low in water, one may regard the solution as one of infinite dilution. The infinite dilution equivalent conductance Λ_0 of the salt may be computed from the λ^+_0 and λ^-_0 values of the ions using Kohlrausch's equation. The solubility of the salt in equivalents per litre is then calculated from the Λ_0 and *K* values. Example 12.20 illustrates the method.

Example 12.20 The specific conductance at 25°C of a suspension of silver chloride in water was determined to be $1 \cdot 826 \times 10^{-6}$ ohm^{-1}. The infinite dilution ionic conductances of Ag$^+$ and Cl$^-$ are 61·92 and 76·34 respectively. Calculate the solubility product of AgCl.
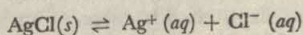
$$AgCl(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$$
$$K_{sp} = [Ag^+\,(aq)]\,[Cl^-\,(aq)]$$

Now, $\Lambda_0 AgCl = \lambda^+_0(Ag^+) + \lambda^-_0(Cl^-) = 61 \cdot 92 + 76 \cdot 34$
$$= 138 \cdot 26 = \Lambda_c \quad \text{(since the value of } c \text{ is small)}$$
$$\Lambda_c = 1000\,k/c$$

or $c = 1000k\Lambda = 10^3 \times \dfrac{1 \cdot 826 \times 10^{-6}}{138 \cdot 26} = 1 \cdot 32 \times 10^{-5}$ eqvt. litre^{-1}

This is the solubility in eqvt. litre^{-1}. Since both Ag$^+$ and Cl$^-$ are singly charged, eqvt. mass = mol. mass and *c* is $1 \cdot 32 \times 10^{-5}$ mol. litre^{-1}. Hence $K_{sp} = c^2 = 1 \cdot 6 \times 10^{-10}$.

12.7.4 Mobilities of Ions

The equivalent conductance of a solution, as mentioned earlier, depends on the number of ions present in the solution and also on the mobility of the ions. Let us turn our attention to the velocity of motion of the ion under an applied potential field. Kohlrausch's law gives specific values for the equivalent conductances of ions in aqueous media. It can be shown that these values are related to the mobilities of these ions. Table 12.3 is an interesting compilation of the mobilities of several ions in aqueous solution, compared to a standard value of 100 for the hydronium ion H_3O^+.

Table 12.3 Relative Mobilities of Ions in Water

Ion	Mobility	Ion	Mobility
H_3O^+	100·00	Cl^-	21·8
Li^+	11·05	Br^-	21·4
Na^+	14·3	I^-	21·9
K^+	21·0	OH^-	56·6
Ca^{2+}	34·0	SO^{2-}_4	45·6

The factors that govern the mobility of an ion in solution are the charge on the ion and the radius of the ion. Since ionic radius increases as we go from Li^+ to K^+ (0·68 to 1·33 A) one would expect the mobility to decrease. Instead, Table 12.3 shows the opposite trend in aqueous solution. This means that Li^+ has a higher radius in water than expected. The reason for this is that ions are solvated to a considerable extent. Li^+ interacts with the solvent water via ion-dipole forces and consequently exists as Li^+ $(H_2O)_6$. Among the univalent cations, Li^+ possesses the strongest hydration sphere around it due to its high charge density. This also explains the order of mobilities.

It is noteworthy that the mobilities of the cation K^+ (radius 1·33 A) and anion Cl^- (radius 1·81 A) are comparable in water despite the difference in their sizes. This is because, in general, hydration of cations is more effective than of anions, due to the orientation difficulty of water molecules around anions. The hydrated K^+ is perhaps of the same size as the hydrated Cl^-.

One would expect, based on the charge density factor considered above, the mobility of H_3O^+ (and to some extent OH^-) to be low. Experiments have shown that the mechanism of conduction by H_3O^+ is not entirely by the individual motion of H_3O^+ ions, but by a transfer of protons from one water molecules of the solvent to another. The rate of proton transfer being much faster than the velocity of H_3O^+, the mobility also becomes high. Similar arguments have been put forward to explain the high mobility of the hydroxide ion.

SUGGESTED READING

S. GLASSTONE, *Electrochemistry*, Van Nostrand, New York, 1942.

W. J. MOORE, *Physical Chemistry*, (3rd Ed.) Prentice Hall Inc., Englewood Cliffs, N.J., 1962.

PROBLEMS

12.1 The specific conductance of 0.02 M of an aqueous solution is 27.7×10^{-4} ohm cm^{-1}. What will be the current when a potential of 2 V is applied across a 50 cm^{-1} long capillary tube of internal diameter of 2 mm filled with KCl solution?

12.2 What is the dissociation constant of water at 25°C if its specific conductance is 6.2×10^{-8} ohm cm^{-1} and $\lambda_c{}^+$ (H$^+$) and $\lambda_0{}^-$ (OH$^-$) are 349.8 and 197.6 ohm^{-1} cm^{-1} eqvt^{-1}?

12.3 The volume of water in an irregular shaped village tank is to be estimated. A chemist suggested to measure its specific conductances before and after adding 500 g of NaCl. Estimate roughly the volume of the tank if the specific conductance before and after the addition of salt is 2.56×10^{-5} and 3.10×10^{-5} ohm cm^{-1} (Λ°NaCl$=149.9$).

12.4 Two electrolytic cells, one containing silver nitrate solution and the other copper sulphate solution were connected in series. After passing a steady current of 1.93 amp it was found that 1.078 g of silver was deposited at the cathode of the first cell. For how long was the current passed and what is the mass of copper deposited in the second cell?

12.5 At the Nangal fertilizer plant in the Punjab, hydrogen is produced by the electrolysis of water. The hydrogen is used for the production of ammonia and nitric acid (by oxidation of ammonia). If the average production of ammonium nitrate is 5000 kg/day, estimate the daily consumption of electricity at the plant.

12.6 During the electrolysis of CrCl$_3$, chlorine gas is evolved at the anode and chromium is deposited at the cathode. How many grams of chromium and how many liters of chlorine (at STP) are produced, when a current of 6.0 amp is passed for one hour?

12.7 From the tables of standard redox potentials calculate the standard potentials of the cells in which the following reactions take place: (a) Sn + Pb^{2+} (aq) $\rightarrow$ Sn^{2+} (aq) + Pb, (b) 2Cr + 3Fe^{2+} (aq) $\rightarrow$ 2Cr^{3+} (aq) + 3Fe, and (c) 2MnO$^-_4$ (aq) + 10Cl$^-$ (aq) + 16H$^+$ (aq) = 2Mn^{2+} (aq) + 5Cl$_2$ + 8H$_2$O.

12.8 Calculate the reduction potentials for the following half-cells.
(a) Mg/Mg^{2+} when [Mg^{2+}] $= 1 \times 10^{-4}$ M
(b) Cl$_2$/Cl$^-$ when [Cl$^-$] $= 2 \times 10^{-5}$ M
(c) Sb/Sb$_2$O$_3$/H$^+$ when [H$^+$] $= 10^{-8}$ M

12.9 Give the voltages of the cells in which the following reactions under the given condition take place.
(a) Mg (s) + Cl$_2$ (1 atm) $\rightarrow$ Mg^{2+} ($10^{-2}M$) + 2Cl$^-$ ($2 \times 10^{-2}M$)
(b) Zn (s) + Fe^{2+} ($10^{-2}M$) $\rightarrow$ Zn^{2+} ($10^{-4}M$) + Fe(s)

12.10 Determine the oxidation number of sulphur in the following H$_2$S, SO$_2$, SF$_6$, SO$_3{}^{2-}$ and S$_2$O$_8{}^{2-}$.

12.11 Determine the oxidation number of chlorine in the following compounds: ICl, ClO, ClO$_2{}^-$, ClO$_4$ and ClO$_2$.

12.12 Nitrogen forms compounds in different oxidation states. Give one example for each possible oxidation state.

12.13 Balance the following equations by the half-cell reaction method:
(a) Cr$_2$O$_7{}^{-2}$ + SO$_3{}^{-2}$ $\rightarrow$ Cr^{3+} + SO$^{-2}_4$ (ACIDIC MEDIUM)
(b) I$_2$ + SO$_2$ $\rightarrow$ SO$^{-2}_4$ + I$^-$ (ACIDIC MEDIUM)
(c) Sn + NO$_3$ $\rightarrow$ SnO$_2$ + NO$_2$ (ACIDIC MEDIUM)
(d) MnO$^-_4$(aq) + SO$_2$ $\rightarrow$ Mn^{2+} (aq) + SO $^{-2}$(aq)   (ACIDIC MEDIUM)

12.14 Balance the following equation by the oxidation number method:
(a) MnO$_2$ + Cl$^-$ (aq) = Mn^{2+} (aq) + Cl$_2$ (ACIDIC MEDIUM)
(b) MnO$_4{}^-$(aq) + SO$_3{}^{-2}$(aq) = MnO$_4{}^{-2}$(aq) + SO$_4{}^{-2}$(aq)   (BASIC MEDIUM)
(c) ClO$^-$ (aq) + Br$^-$ (aq) = BrO$^-_3$ (aq) + Cl$^-$ (aq)   (BASIC MEDIUM)
(d) Zn + NO$_3{}^-$ (aq) = Zn^{2+} (aq) + NH$_4{}^+$ (aq)   (ACIDIC MEDIUM)

12.15 What volume of 1·36 *M* copper sulphate solution will react with 0·654 g of zinc?

12.16 40 ml of 0·3 *M* solution of hydrogen peroxide oxidises 32 ml of NaI solution to I_2. What is the molarity of sodium iodide solution?

12.17 0·93 g of $KMnO_4$ sample is dissolved in water and the solution is made up to 100 mL. 20 ml of *M*/20 oxalic acid on titration in acidic medium requires 21·5 ml of the above solution. Estimate the percentage of MnO_2 in the given sample of the permanganate.
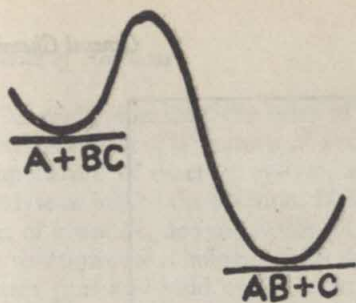
Kinetics and Mechanisms of Reactions

Only in time can the moment in the rose-garden,
The moment in the arbour where the rain beat,
The moment in the draughty church at smoke fall
Be remembered; involved with past and future.
Only through time time is conquered.

Four Quartets—T. S. ELIOT

Since 'tis Nature's law to change
Constancy alone is strange

EARL OF ROCHESTER

A knowledge of the free energy changes involved in a given process tells us whether the process will occur or not. However, neither the thermodynamic data nor the stoichiometry of a chemical reaction can tell us about how fast or how slow the reaction proceeds. For example, the oxidation of carbon (graphite) to yield CO_2 gas has a $\Delta G°$ of -94 kcal mol^{-1} at 298 K, suggesting that the oxidation is highly favoured. Yet, graphite can be kept in contact with air indefinitely and the oxidation does not seem to occur. Obviously, the oxidation reaction is extremely slow at 298 K. Likewise, we saw from the phase diagram of carbon (Chapter 10, Fig. 10.5), that diamond should get converted to graphite, a physical change. Here again while the conversion is predicted to occur spontaneously, the speed with which it happens is extremely slow. On the other hand, there are other reactions such as oxidation of natural gas (burning in air as in a Bunsen burner) that are very fast.

Many chemical reactions proceed with measurable rates as shown in Fig. 13.1 (the decomposition of N_2O_5 into NO_2 and O_2). Even though this decomposition reaction appears to be simple and straightforward, the reaction actually takes place in several steps. Measuring the rate of such a reaction is useful to understand these steps (*mechanism*).
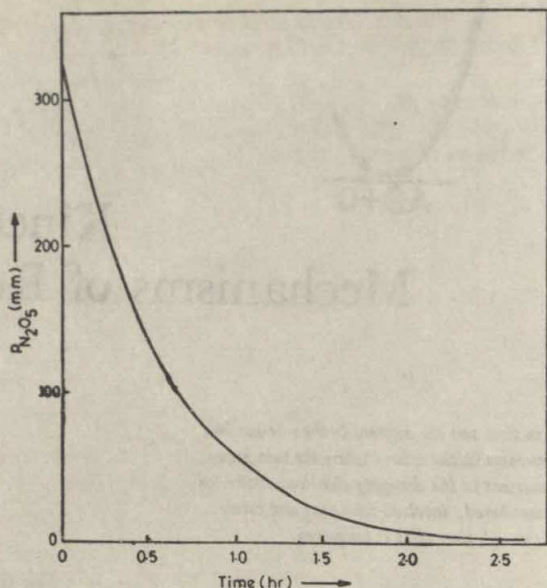
Fig. 13.1 Variation in the concentration of N_2O_5 with time in the first-order decomposition reaction at 45°C $2N_2O_5 \rightarrow 4NO_2 + O_2$

Consider the simple reaction involving the reduction of IO^-_3 by sulphite ions in acid medium. The following three steps are of importance in this reaction:

(1) $IO^-_3 + 3SO^{2-}_3 \rightarrow I^- + 3SO^{2-}_4$ (SLOW)

(2) $5I^- + 6H^+ + IO_3^- \rightarrow 3H_2O + 3I_2$ (FAST)

(3) $I_2 + SO^{2-}_3 + H_2O \rightarrow SO^{2-}_4 + 2I^- + 2H^+$ (VERY FAST)

If a calculated amount of sulphite is added to a solution containing excess of iodate ion, reaction (1) will first occur followed by reaction (2). The iodine from reaction (2) reacts with sulphite ions to give iodide and sulphate ions until the sulphite ions are exhausted. The iodide ion from reactions (1) and (3) will further react with the excess IO^-_3 in solution and produce iodine. Since no sulphite ions are present in solution, iodine cannot be used for any reaction and the solution will turn purple in the presence of the starch indicator. This is a *clock reaction* since the reaction rate can be timed by the sudden appearance of the purple colour.

Chemists try to control rates of reactions by changing the factors affecting the rates. For example consider the dehydration of ethyl alcohol, C_2H_5OH. The dehydration gives ethylene, C_2H_4, or diethyl ether, $C_2H_5OC_2H_5$, depending on the conditions:

$$C_2H_5OH \xrightarrow{\text{conc. } H_2SO_4} C_2H_4 + H_2O$$

$$2C_2H_5OH \xrightarrow{\text{dil. } H_2SO_4} C_2H_5OC_2H_5 + H_2O$$
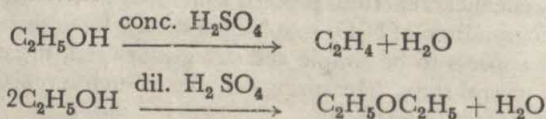
At higher temperatures, ethylene is formed faster than diethyl ether.

Generally speaking, the rates of chemical reactions are affected by the following variables: (*i*) nature of reactants, (*ii*) concentration of reactants, (*iii*) temperature of reacting system, and (*iv*) presence of additives which may catalyse or inhibit the reaction. If the reaction is heterogenous as in the combustion of graphite, decomposition of an oxide or dissolution of a metal in acid, the reaction rate is influenced by the *phase boundary* (interface) between the two phases (gas and solid or liquid and solid). A large surface area of the solid would favour such *heterogenous reactions*. Study of rates or velocities with which chemical processes occur and the conditions governing the rates is termed *chemical kinetics*. In this chapter, we shall discuss rates of a variety of chemical reactions and the factors controlling rates and then examine how rate data can be employed to understand mechanisms of reactions.

13.1 REACTION RATES AND RATE LAWS

In Fig. 13.2 we have shown the general behaviour of the concentration of a reactant and a product as a reaction proceeds. The concentrations change relatively faster at first and then more slowly. The rate of change of concentra-
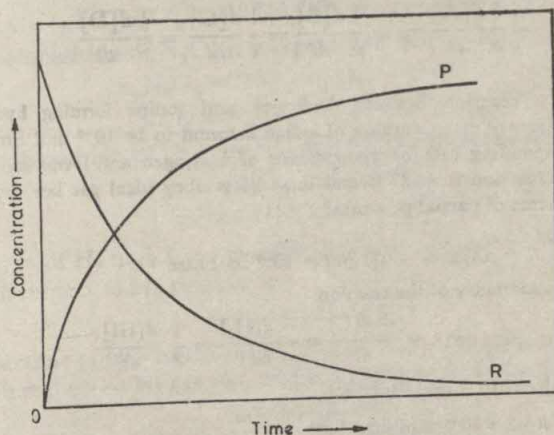
Fig. 13.2 Variation in the concentrations of reactant (*R*) and product (*P*) with time in a first-order reaction

tion of the reactant which is given by the slope of the concentration-time curve also decreases with time. The rate of change of concentration, also called the *rate of reaction*, is the change in concentration of a reactant or product per unit time and is generally expressed as a time derivative, dc/dt.

13.1.1 Rate Expressions
Let us consider the simple gaseous reaction,
$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$
The rate of this reaction is given by the rate of disappearance of one of the reactants N_2 or O_2. We can express this as
$$\text{RATE OF REACTION} = -d[N_2]/dt = -d[O_2]/dt$$
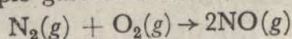
Where, $d[N_2]/dt$ and $d[O_2]/dt$ are both negative since the concentration decreases with time and the reaction rate itself will be positive as it should be. The reaction rate could also be expressed as the rate of formation of NO, $d[NO]/dt$, which is a positive quantity. Because of the stoichiometry of the reaction, for every mol of N_2 or O_2 reacting, we get two moles of NO. The rate of formation of NO will work out to be twice the rate of disappearance of N_2. In order to avoid this difference between the two rates, we generally divide the rate of reaction (defined with respect to individual reactants or products) by the number of moles involved in the reaction. In the present example, we will have,

$$-\frac{d[N_2]}{dt} = -\frac{d[O_2]}{dt} = +\frac{1}{2}\frac{d[NO]}{dt}$$

REACTION RATE $=$ RATE OF DISAPPEARANCE of N_2 or O_2

$=\frac{1}{2}$ (RATE OF FORMATION OF NO)

For a general reaction,

$$aA + bB \rightarrow cC + dD$$
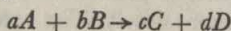
we can write the reaction rate as

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Example 13.1 In a reaction between hydrogen and iodine forming hydrogen iodide $(H_2 + I_2 \rightarrow 2HI)$ the rate of disappearance of iodine is found to be 10^{-6} mol litre^{-1} s^{-1}. What would be the corresponding rate of disappearance of hydrogen and formation of hydrogen iodide? Also, if the reaction is at 27°C and these gases obey ideal gas law, how would you express the rate in terms of partial pressures?

$$\text{RATE} = -d[I_2]/dt = 10^{-6} \text{ mol litre}^{-1} \text{ s}^{-1}$$

According to the stoichiometry of the reaction

$$\text{RATE} = \frac{-d[I_2]}{dt} = \frac{-d[H_2]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}$$

Therefore, $-d[H_2]/dt = 10^{-6}$ mol litre^{-1} s^{-1}

and $d[HI]/dt = 2 \times 10^{-6}$ mol litre^{-1} s^{-1}

From the ideal gas law we have, $p = nRT/V$

The pressure equivalent of 10^{-6} mol litre^{-1} is

$$P = 10^{-6} \times 0.082 \times 300 = 2.46 \times 10^{-5} \text{ atm}$$

$$\text{Rate} = 2.46 \times 10^{-5} \text{ atm s}^{-1}$$

As early as 1864, Guldberg and Waage realised that the rate of a homogeneous reaction is proportional to some power of the concentrations of the reactants; the concentrations themselves in homogeneous phase are expressed in moles per litre. For the general reaction considered above,

$$\text{RATE} \propto [A]^x [B]^y$$

or, $$\text{RATE} = k[A]^x [B]^y$$

where k is the proportionality constant. This manner of mathematically expressing reaction rates is called the *rate law*. The numerical values of x and y can be determined experimentally, but cannot be deduced from the overall

reaction or in any other manner. The values of x and y need not be the same as the stoichiometric coefficients a and b.

The proportionality constant k in the above equation is called the *specific rate constant* of the reaction. The unit of k depends on the unit employed for concentration and the unit of time; k has a specific value at a given temperature. Specific rate constants of reactions provide the basis for a quantitative comparison of the reaction rates. The sum of the powers of the concentration terms (x and y) in the rate equation is known as the *order of the reaction*. While $x+y$ gives the overall order of the reaction, x and y individually give the orders with respect to the reactants A and B respectively. We can, thus, state that the reaction is of x-order with respect to A.

The orders of reactions provide the basis for classifying reactions. Generally, the order of a reaction can be anywhere between zero and three. A *zero-order reaction* is one where the reaction rate does not depend on the concentration of the reactant; or the rate is proportional to the zeroth power of the concentration of the reactant. Such reactions are not common. Decomposition of N_2O on a hot platinum surface is an example of a zero-order reaction.
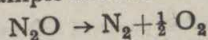
$$N_2O \rightarrow N_2 + \tfrac{1}{2} O_2$$
$$\text{RATE} \propto [N_2O]^0$$
$$\text{RATE} = -d[N_2O]/dt = k[N_2O]^0 = k = \text{CONSTANT}$$

The decomposition of N_2O_5 is a typical *first-order reaction:*
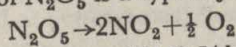
$$N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2} O_2$$
$$\text{RATE} = -d[N_2O_5]/dt = k[N_2O_5]$$

The decomposition of NO_2 to NO and O_2 is a *second-order reaction:*
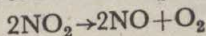
$$2NO_2 \rightarrow 2NO + O_2$$
$$\text{RATE} = k[NO_2]^2$$

The reaction of H_2 and I_2 to give HI is also a second-order reaction, and the order with respect to H_2 or I_2 is one.

$$\text{RATE} = k[H_2][I_2]$$

The reaction of NO and oxygen to give NO_2 is a *third-order reaction*, but the order with respect to NO is two and the order with respect to oxygen is one.
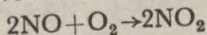
$$2NO + O_2 \rightarrow 2NO_2$$
$$\text{RATE} = k[NO]^2[O_2]$$

We had mentioned earlier that there is no relation between the order (exponents in the rate equation) and the stoichiometric coefficients in the reaction. An example to illustrate this point would be the reaction between decaborane and ethyl alcohol to form triethyl borate and hydrogen:
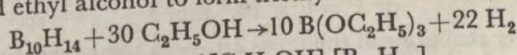
$$B_{10}H_{14} + 30\ C_2H_5OH \rightarrow 10\ B(OC_2H_5)_3 + 22\ H_2$$
$$\text{RATE} = k[C_2H_5OH][B_{10}H_{14}]$$

The overall order of this reaction is two, but the reaction is first order with respect to either reactant.

Orders of reactions need not always have integral values. For example, the decomposition of acetaldehyde into CH_4 and CO under certain conditions is of 1·5 order.
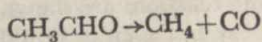
$$CH_3CHO \rightarrow CH_4 + CO$$
$$\text{RATE} = k[CH_3CO]^{1·5}$$

The seemingly simple gas phase reaction between H_2 and Br_2 to form HBr is found to obey the complex rate law,

$$\text{RATE} = \frac{d[\text{HBr}]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + k'\{[\text{HBr}]/[Br_2]\}}$$

In this case, there is no clear indication of reaction order. We shall later show how the concept of reaction order loses significance in reactions such as the HBr reaction, where a number of reactions occur simultaneously.

Example 13.2 Rate equations of three reactions are given below. Find the overall reaction order from the inspection of the rate equations.

Reaction	*Rate equation*
(a) $2NO + H_2 \rightarrow N_2O + H_2O$	$\text{RATE} = k[NO]^2[H_2O]$
(b) $H_2C=CH-CH=CH_2 + H_2C=CH_2$	
$\rightarrow$ cyclohexene	$\text{RATE} = k[\text{ethylene}][\text{butadiene}]$
(c) $H_2O_2 + 2H^+ + 3I^-$	
$\rightarrow I_3^- + 2H_2O$	$\dfrac{d(I_3)^-}{dt} = k[H_2O_2][I^-] + k'[H_2O_2][I^-][H^+]$

(a) Since the rate depends on the second power of NO and first power of hydrogen, the reaction is of, $2 + 1 = 3$, i.e., third-order.

(b) Since the rate is dependent on first powers of both ethylene and butadiene, order of the reaction is 2.

$$\frac{d\,(\text{cyclohexene})}{dt} = k\,[\text{ethylene}]^1\,[\text{butadiene}]^1$$

$$\text{Order} = 1 + 1 = 2$$

(c) This reaction cannot be ascribed a simple order, because we cannot write a simple rate expression as in the previous cases.

As mentioned earlier, the unit of the specific rate constant depends on the unit of concentration and time employed. In the case of a simple first-order reaction, like $A \rightarrow$ products, rate $= k[A]$. If the rate of decrease of the concentration of A is 10^{-5} mol litre^{-1} s^{-1} when the concentration of A is 10^{-3} mol litre^{-1},

$$\text{RATE} = 10^{-5} \text{ mol litre}^{-1} \text{ s}^{-1} = k\,[10^{-3} \text{ mol litre}^{-1}]$$
$$\text{or } k = 10^{-2} \text{ s}^{-1}$$

If the concentration is expressed in mol cm^{-3} instead of mol litre^{-1}, the concentration of A will be 10^{-6} mol cm^{-3} and the rate will be 10^{-8} mol cm^{-3} s^{-1}. The value of k will still be 10^{-2} s^{-1}. However, if the rate is expressed in mol litre^{-1} min^{-1} and concentration in mol litre^{-1}, then,

$$\text{RATE} = 10^{-5} \times 60 \text{ mol litre}^{-1} \text{ min}^{-1} = k\,[10^{-3} \text{ mol litre}^{-1}]$$
$$\text{or } k = 6 \times 10^{-1} \text{ min}^{-1}$$

In second-order reactions of the type, $2A \rightarrow B$, the rate expression is,

$$\text{RATE} = k\,[A]^2$$
$$\text{mol litre}^{-1} \text{ s}^{-1} = k\,[\text{mol litre}^{-1}]^2$$

The rate constant will, therefore, have the unit litre mol^{-1} s^{-1}. The rate constant in a third-order reaction can be similarly shown to have the unit litre^2 mol^{-2} s^{-1}. A reaction of nth order will have the unit litre$^{(n-1)}$ mol$^{-(n-1)}$ s^{-1}.

The rate constants of some reactions are shown in Table 13.1. We see that some of the reactions are very fast even in liquid phase. This is because the reacting species like H_3O^+ and OH^- diffuse very fast through water. In many

reactions taking place in solution phase, the solvent plays a crucial role. While in gas phase the reacting species can encounter each other by direct collision, in solution phase such encounters are decreased by the solvent molecules.

Table 13.1 Typical Rate Constants of Chemical Reactions

Order	Reaction	Phase	Temp.	k
First	$2N_2O_5 \rightarrow 4NO_2 + O_2$	gas	23°C	4.0×10^{-5} s^{-1}
	$H_2O \rightarrow H^+ + OH^-$	liquid	25°C	2.6×10^{-5} s^{-1}
	$C_2H_5Cl \rightarrow C_2H_4 + HCl$	gas	23°C	5.9×10^{-30} s^{-1}
Second	$H_2 + I_2 \rightarrow 2HI$	gas	300°C	1.3×10^{-4} litre mol^{-1} s^{-1}
	$2HI \rightarrow H_2 + I_2$	gas	300°C	2.5×10^{-6} litre mol^{-1} s^{-1}
	$H^+ + OH^- \rightarrow H_2O$	liquid	25°C	1.5×10^{11} litre mol^{-1} s^{-1}
	$H_3O^+ + F^- \rightarrow HF + H_2O$	liquid	25°C	1×10^{11} litre mol^{-1} s^{-1}
	$CH^+_4 + CH_4 \rightarrow CH^+_5 + CH_3$	gas	25°C	5.11×10^{11} litre mol^{-1} s^{-1}
	$Ne^+ + H_2 \rightarrow NeH^+ + H$	gas	25°C	2.05×10^{11} litre mol^{-1} s^{-1}
Third	$H + H + H_2 \rightarrow H_2 + H_2$	gas	25°C	5×10^9 litre^2 mol^{-2} s^{-1}
	$N + N + N_2 \rightarrow N_2 + N_2$	gas	25°C	1.4×10^9 litre^2 mol^{-2} s^{-1}

In spite of this factor, some reactions in solution take place with relative ease since the products formed are energetically favoured. An extreme caes of such reactions is the recombination of iodine atoms to form I_2 in a solution of CCl_4. Once the two iodine atoms encounter each other (come close to each other), the reaction proceeds spontaneously with release of energy.

Example 13.3 Rate constants of three reactions are given in the following table. Convert these rate constants to units as indicated.

Reaction	Order	Rate constant	Change the units to
(a) $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2} O_2$	First	0.004 s^{-1}	hr^{-1}
(b) $NH^-_2 + N_2H^+_5 \rightarrow NH_3 + N_2H_4$	Second	7.9×10^7 litre mol^{-1} s^{-1}	cc molecule^{-1} s^{-1}
(c) $H + H + H_2 \rightarrow H_2 + H_2$	Third	5×10^9 litre^2 mol^{-2} s^{-1}	cc^2 mol^{-2} min^{-1}

(a) In order to find out the specific rate constant in hr^{-1}, one needs to multiply the value of k in s^{-1} by 60×60.

$$k = 0.004 \text{ s}^{-1} = 0.004 \times 60 \times 60 \text{ hr}^{-1} = 1.44 \text{ hr}^{-1}$$

(b) To convert litre to cc we multiply by 10^3 and to change mol^{-1} to molecule^{-1} we divide by Avogadro number. Therefore,

$$k = 7.9 \times 10^7 \text{ litre mol}^{-1} \text{s}^{-1} = \frac{7.9 \times 10^7 \times 10^3}{6.02 \times 10^{23}} \text{ cc molecule}^{-1} \text{s}^{-1}$$

$$= \frac{7.9}{6.02} \times 10^{-13} \text{ cc molecule}^{-1} \text{s}^{-1}$$

(c) In order to change litre^2 to cc^2 we multiply by $10^3 \times 10^3$ and to change s^{-1} to min^{-1} we multiply by 60.

$$k = 5 \times 10^9 \text{ litre}^2 \text{ mol}^{-2} \text{s}^{-1}$$
$$= 5 \times 10^9 \times 10^3 \times 10^3 \times 60 \text{ cc}^2 \text{ mol}^{-2}\text{min}^{-1}$$
$$= 3 \times 10^{17} \text{ cc}^2 \text{ mol}^{-2} \text{min}^{-1}$$

Example 13.4 N_2O_5 decomposes according to the equation,
$$2N_2O_5 \rightarrow 4NO_2 + O_2$$
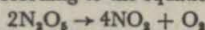
(i) The rate can be expressed as
$$-d[N_2O_5]/dt = k_1[N_2O_5]; \quad d[NO_2]/dt = k_2[N_2O_5] \text{ and } d[O_2]/dt = k_3[N_2O_5].$$
How are k_1, k_2 and k_3 related?

(ii) In a solution of carbon tetrachloride, the following rate data are obtained at 30°C:

Conc. of $[N_2O_5]$	Rate of decomposition
0·34 mol litre^{-1}	0·10 mol litre^{-1} hr^{-1}
0·68	0·20
1·36	0·40

(a) Write the rate equation and indicate the order of the reaction.
(b) Calculate the rate constant at 30°C.
(c) Calculate the rate of decomposition at 30°C if $[N_2O_5] = 0.20$ mol litre^{-1}.

(i) From the stoichiometry of the reaction, we can readily see that $k_2 = 2k_1$ and $k_3 = \frac{1}{2}k_1$.

(ii) (a) rate $= -d[N_2O_5]/dt = k[N_2O_5]$

Since the rate is proportional to the first power of the concentration of N_2O_5, the order of reaction is one (first order).

(b) $k = \dfrac{\text{rate}}{[N_2O_5]} = \dfrac{0.10 \text{ mol litre}^{-1} \text{ hr}^{-1}}{0.34 \text{ mol litre}^{-1}} = \dfrac{0.20}{0.68} = \dfrac{0.40}{1.36}$

$k = 0.29$ hr^{-1}

(c) rate $= -d[N_2O_5]/dt = -0.29$ hr^{-1} $[N_2O_5]$
$$= 0.29 \text{ hr}^{-1} \times 0.20 \text{ mol litre}^{-1} = 0.058 \text{ mol litre}^{-1} \text{ hr}^{-1}$$

Example 13.5 For a gaseous reaction $A_2 + 2B \rightarrow 2AB$, the following rate data are obtained at 250 K:

Rate of disapperance of A_2 $-d[A_2]/dt$ (mol/litre sec)	Concentration (mol/litre)	
	$[A_2]$	$[B]$
1·2 × 10⁻³	0·10	0·01
4·8 × 10⁻³	0·10	0·04
2·4 × 10⁻³	0·20	0·01

Calculate the rate constant for the reaction and rate of formation of AB when $[A_2] = 0.02$ and $[B] = 0.01$ at 250 K.

We see that when concentration of A_2 is constant and the concentration of B is increased four-times, the rate also increases four-times; rate is proportional to $[B]$. When the concentration of B is constant and the concentration of A_2 is doubled, the rate is also doubled, or rate is proportional to $[A_2]$. The rate equation is, therefore, given by,

$$-\frac{d[A_2]}{dt} = k[A_2][B]$$

$$k = \frac{-d[A_2]/dt}{[A_2][B]} = \frac{1.2 \times 10^{-3}}{0.1 \times 0.01} = \frac{4.8 \times 10^{-3}}{0.10 \times 0.04} = \frac{2.4 \times 10^{-3}}{0.20 \times 0.01} = 1.2 \text{ litre mol}^{-1} \text{ s}^{-1}$$

From the stoichiometry of the reaction,

$$\text{Rate of formation of } AB = \frac{d[AB]}{dt} = 2 \times \frac{d[A_2]}{dt} = 2 \times k[A_2][B]$$

$$= 2 \times 1.2 \frac{\text{litre}}{\text{mol s}} \times 0.02 \frac{\text{mol}}{\text{litre}} \times 0.01 \frac{\text{mol}}{\text{litre}}$$

$$= 4.8 \times 10^{-4} \text{ mol litre}^{-1} \text{ s}^{-1}$$

13.1.2 Integration of Simple Rate Expressions

The differential rate expressions discussed till now show how reaction rates depend on the concentrations of reactants. If we have to find out how the concentrations depend on time, we need to integrate the differential rate expressions. For the first-order reaction, $A \rightarrow B$, the differential rate expression is

$$\text{RATE} = -d[A]/dt = k[A]$$

This relation can also be written as

$$-d[A]/[A] = -dc/c = k\,dt$$

where $[A]$ is replaced by concentration c. On integration, we get,

$$\int_{c_0}^{c} -\frac{dc}{c} = \int_0^t k\,dt$$

Here c_0 is the concentration at time, $t = 0$.

$$[-\ln c]_{c_0}^{c} = k[t]_0^t$$

$$-\ln \frac{c}{c_0} = kt \text{ or } c = c_0\, e^{-kt}$$

According to the above relation, the logarithm of the reactant concentration linearly decreases with time. If we plot $\ln c$ against t, we will get a straight line with a slope of $-k$, or a straight line plot of $\log c$ against t will have a slope of $-k/2 \cdot 303$. A typical plot of $\ln c$ against time in the case of the first-order decomposition of N_2O_5 is shown in Fig. 13.3
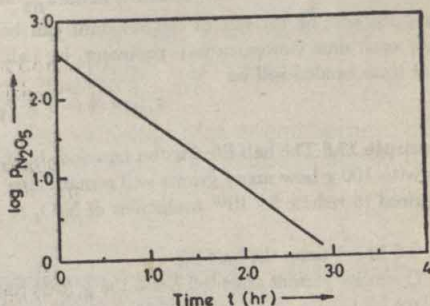
Fig. 13.3 Plot of logarithm of concentration of N_2O_5 against time in the first-order decomposition of N_2O_5

By a similar procedure we can derive the integrated form of the rate expression for second-order reactions. In a second-order reaction of the type $2A \rightarrow B$;

$$\text{RATE} = \frac{-d[A]}{dt} = k[A]^2$$

$$-dc/dt = kc^2 \text{ or } -dc/c^2 = k\,dt$$

On integration, we will get

$$1/c - 1/c_0 = kt$$

In such a case, a plot of $1/c$ against t would be a straight line with slope k.

13.1.3 Half-life for First-order Reactions

A quantitative measure of the rate of a reaction is provided by the *half-life* of the reaction, which is defined as the time required for one half of the quantity

of a reactant to react. Thus, if we start with a concentration of 1·0 mol litre^{-1} of a reactant, the time needed for the concentration to become 0·5 mol litre^{-1} is half-life of the reaction.

For a first-order reaction, $- \ln c/c_0 = kt$. Substituting $c = c_0/2$,

$$- \ln[(c_0/2)/c_0] = \ln 2 = k\, t_{1/2}$$

where $t_{1/2}$ is the half-life. This can be further simplified to

$$2·303 \log 2 = 0·693 = k\, t_{1/2}$$

or

$$t_{1/2} = 0.693/k$$

If we know the value of k, we can calculate $t_{1/2}$ and vice versa. We see that the expression for half-life does not include any concentration term; $t_{1/2}$ of a first-order reaction is therefore concentration-independent and is characteristic of the reaction. The half-life of a second-order reaction, however, depends on the initial concentration of the reactant.

Example 13.6 For a certain reaction it takes 5 minutes for the initial concentration of 0·5 mol litre^{-1} to become 0·25 mol litre^{-1} and another 5 minutes to become 0·125 mol litre^{-1}. What is the specific rate constant of the reaction?

Since the half-life is independent of the initial concentration, the reaction is of first order. For a first-order reaction

$$t_{1/2} = 0·693/k \text{ or } k = 0·693/t_{1/2}$$

In the present reaction $t_{1/2} = 5$ minutes, hence $k = 0·693/5 = 0·138$ min^{-1}.

Example 13.7 For a first-order reaction having a specific rate constant of 69·3 sec^{-1}, how long will it take for 1 mol litre^{-1} of the reactant to reduce to $1/16$ mol litre^{-1}?

$$k = 69·3 \text{ s}^{-1}, \text{ hence } t_{1/2} = 0·693/69·3 = \tfrac{1}{100} \text{ s.}$$

Disappearance of 15/16th of the reactant can be viewed as loss in four steps: 1/2, 1/4, 1/8, 1/16, each time concentration reducing by half. Since four half-life times are involved, the total time needed will be

$$t_{1/2} \times 4 = 4 \times (\tfrac{1}{100}) = \tfrac{1}{25} \text{ s}$$

Example 13.8 The half-life for the reaction, $N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2} O_2$ is 2·4 hr at 30°C. (a) Starting with 100 g how many grams will remain after a period of 9·6 hr? (b) What time would be required to reduce 5×10^{10} molecules of N_2O_5 to 10^8 molecules?

(a) 9·6 hr = 4 times the half-life

Quantity present after 9·6 hrs = 100 g (0·5) (0·5) (0·5) (0·5) = 6·3 g

(b) 10^8 molecules = 5×10^{10} molecules $(0·5)^{t/t_{1/2}} = 5 \times 10^{10} (0·5)^{t/2·4}$

$$t = 22 \text{ hr}$$

Table 13.2 shows the integrated rate expressions, units of the rate constants, and the half-life times for reactions of various orders.

13.1.4 Reaction Rates and Equilibria

We have mentioned in our discussion of equilibria (Chapter 10), that in a state of equilibrium, the rate of the forward and reverse reactions are equal. In the equilibrium reaction,
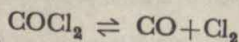
$$COCl_2 \rightleftharpoons CO + Cl_2$$

the rate of the forward reaction, $COCl_2 \rightarrow CO + Cl_2$ is given by

$$(\text{RATE})_{\text{forward}} = k_f [COCl_2]$$

Table 13.2 Integrated Rate Expressions, Units of the Rate Constants, and Half-life Times for Reactions of Various Orders

$$\text{Rate} = -d[A]/dt = k[A]^n$$

where $[A]$ is the concentration of reactant A in mol litre^{-1} at time t in seconds, A_0 the concentration of reactant A at $t=0$, and n the order of the reaction with respect to A.

Order, n	Integrated rate expression	Units of rate constant, k	half-life, $t_{1/2}$
0	$[A_0] - [A] = kt$	mol litre^{-1} s^{-1}	$[A_0]/2k$
1	$2 \cdot 303 \log \dfrac{[A_0]}{[A]} = kt$	s^{-1}	$0 \cdot 693/k$
2	$\dfrac{1}{[A]} - \dfrac{1}{[A_0]} = kt$	litre mol^{-1} s^{-1}	$\dfrac{1}{[A_0]k}$
3	$\frac{1}{2} \left\{ \dfrac{1}{[A]^2} - \dfrac{1}{[A_0]^2} \right\} = kt$	litre^2 mol^{-2} s^{-1}	$\dfrac{3}{2k[A_0]^2}$
n $(n \neq 1)$	$\dfrac{1}{(n-1)} \left\{ \dfrac{1}{[A]^{n-1}} - \dfrac{1}{[A_0]^{n-1}} \right\} = kt$	litre^{n-1} mol$^{-(n-1)}$ s^{-1}	$\dfrac{(2^{n-1} - 1)}{k[n-1][A_0]^{n-1}}$

The rate of the reverse reaction, $CO + Cl_2 \rightarrow COCl_2$ is,

$$(\text{RATE})_{\text{reverse}} = k_r[CO][Cl_2]$$

At equilibrium

$$(\text{RATE})_{\text{forward}} = (\text{RATE})_{\text{reverse}}$$

$$k_f[COCl_2] = k_r[CO][Cl_2]$$

or,
$$\frac{k_f}{k_r} = \frac{[CO][Cl_2]}{[COCl_2]} = K$$

where K is the equilibrium constant. This principle that at equilibrium, each process is exactly balanced by the reverse process, is sometimes referred to as the *principle of microscopic reversibility*.

13.1.5 Complex Rate Laws

In section 13.1.1 we pointed out that the reaction, $H_2 + Br_2 \rightarrow 2HBr$, follows a complex rate law. Such reactions result from a series of steps, none of which entirely determines the rate of the reaction. The complex rate expression in the case of the HBr reaction results from the following steps.

$$Br_2 \rightarrow 2\,Br$$
$$Br + H_2 \rightarrow HBr + H$$
$$H + Br_2 \rightarrow HBr + Br$$
$$H + HBr \rightarrow H_2 + Br\cdot$$
$$2Br \rightarrow Br_2$$
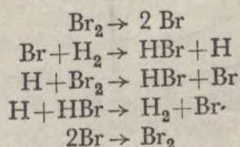
This is an example of a *chain reaction* where the first step generates the highly reactive intermediate, Br. Once the chain is initiated, it is kept 'alive' by *propagation reactions*. The last step is an example of *chain termination*, where the reactive chain carriers are quenched or ' killed '.

There are many reaction systems where a reactant participates in more than one reaction occurring simultaneously as shown below.

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$
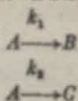
If both these reactions are of first order, then

$$-d[A]/dt = k_1[A] + k_2[A] = k[A]$$

where $k = k_1 + k_2$, and hence,

$$\ln \frac{[A_0]}{[A]} = kt \quad \text{or} \quad [A] = [A_0]e^{-kt}$$

we can also see that $\quad [B] = k_1[A] = k_1[A_0]e^{-kt}$

and $\quad [C] = k_2[A] = k_2[A_0]e^{-kt}$

There are also reactions where the product formed in a reaction further reacts to form a new product:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
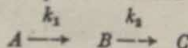
Again, assuming the convenient case of each step to be first order:

$$-d[A]/dt = k_1[A]$$
$$d[B]/dt = k_1[A] - k_2[B]$$

and $\qquad\qquad\qquad d[C]/dt = k_2[B]$

The kinetic plots of these two reactions are given in Fig. 13.4.
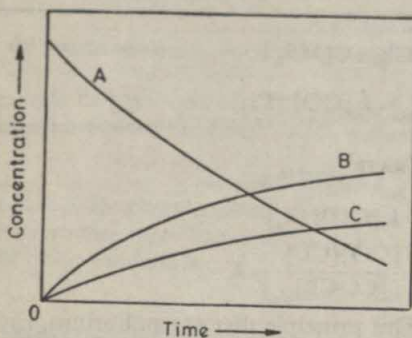
Fig. 13.4 (*a*) Variation of the concentrations of reactant A, and products B and C, with time for the simultaneous reaction
$$A \begin{smallmatrix} \nearrow B \\ \searrow C \end{smallmatrix}$$
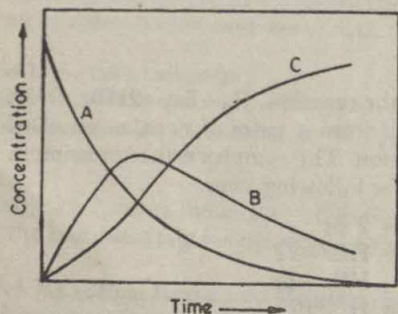
Fig. 13.4 (*b*) Time dependence of the concentrations of species in a consecutive reaction $A \to B \to C$

13.2 EXPERIMENTAL DETERMINATION OF REACTION RATES

The study of chemical *kinetics* deals with the information on the concentrations of reactants or/and products as a function of time. In principle, any method

which has the capability of measuring the concentration of the chemical species has the potential for becoming a tool for experimental studies in kinetics. Two factors determine whether or not a experimental method of studying kinetics in a specific chemical reaction is satisfactory. These are, selectivity of the analytical method, and the average time needed for measurement.

In selecting an analytical method one must find out whether the reactant and product of interest can be analysed by the method at all and to what extent the other species present in the reaction system would cause interference. In many simple systems, rates are indeed determined by simple quantitative analytical procedures like volumetry. Very often, however, the entity that is experimentally measured is not the concentration directly, but a property that varies linearly with concentration. For example, in the hydrolysis of cane sugar (sugar) into glucose and fructose, the reaction rate is studied by following the optical rotation of the reaction mixture (extent to which the plane of polarized light is rotated). This is done with the help of a *polarimeter*.

In solution phase, where most chemical reactions are carried out, *absorption spectroscopy* is commonly employed to determine the concentration of reactants or products. One generally makes use of characteristic absorption bands in the infrared, visible or ultraviolet absorption spectrum either of the reactant or the product and follows the absorbance as a function of time. Absorbance is the product of absorptivity or extinction coefficient ϵ, optical path length or length of the cell, l, and concentration, c:

$$\text{ABSORBANCE} = \epsilon lc \qquad \text{(BEER'S LAW)}$$

Since ϵ is a constant for a particular substance at a fixed wavelength and l is kept constant in an experiment, the measured absorbance is directly proportional to the concentration. Other methods such as *NMR spectroscopy* can also be used for rate studies by measuring the signal due to a particular group in the reactant or product as a function of concentration.

In gas phase, experiments are somewhat more difficult for a number of reasons. Firstly, gaseous reactants and products are difficult to handle. Since it is almost always necessary to do experiments at pressures other than atmospheric pressure, one needs specialised apparatus, be they for high pressures or for very low pressure. Secondly, gases being dilute assemblies of particles, even to do a simple absorption spectroscopic experiment, the absorption cell has to provide a much longer optical path length because of low values of concentration of the absorbing species. Once this problem of concentration is tackled, any physical method can, in principle, be employed to study gas kinetics. In simple decomposition or other reactions where a gas is evolved in the reaction, one could use a manometer to measure gas pressures and these pressures directly give the concentrations. For example, the decomposition of cyclopentene to cyclopentadiene and hydrogen can be studied by measuring the pressure of hydrogen. The decomposition of a metal oxide to metal and oxygen, can similarly be studied manometrically.

Having established the method for determining the concentrations of reactants or products, it is an easy matter to fit the data into one of the rate laws. For example, if a plot of the logarithm of concentration against time is linear, the reaction is first order. A simple way of determining order is to take a series of mixtures containing the two reactants A and B where the concentration of one of them (say, B) is kept constant. The initial rate of reaction is determined with all the mixtures by noting the change in the concentration of A

(or of a product) after a small time interval. Since only the initial concentration of A is different in the different mixtures, the initial rate should vary as $[A]^n$ where n is the reaction order. Thus, if the rate also doubles when the concentration of A is doubled, the reaction is first order.

In recent years, rates of fast reactions have been studied by a variety of techniques, based mainly on spectroscopy. It is not hard to visualise the ingenuity required to study reactions which are complete within microseconds (10^{-6} s) or less (see section 13.11).

13.3 MECHANISMS OF REACTIONS

Rate data are valuable in obtaining a complete description of how reactant molecules are transformed into products. In a sense, rate data mainly provide negative information regarding *reaction mechanisms*. Good kinetic data allow us to reject several possible alternative mechanisms of a reaction if those mechanisms do not agree with observations. Even if we work out a mechanism that fits with the rate data, we cannot be certain that the mechanism is correct. It only means that the mechanism is consistent with the kinetic observations. It is quite possible that there are other mechanistic routes, possibly unfamiliar to us, which may show equally good agreement with the rate data. Chemists have investigated the kinetics of ever so many reactions that we now have a fairly good idea about the mechanisms of various classes of reactions. Such proven mechanisms have provided consistent and satisfactory descriptions of chemical reactions and have enabled chemists to predict mechanisms in new chemical systems under similar reaction situations.

Most reactions do not proceed by a single-step conversion of the reactants to products. The reactions may proceed in several steps involving one or more reaction *intermediates*. These intermediates may be long-lived or short-lived. The rate of such a multi-step reaction is determined by the slowest step or the *rate-determining step* just as the rate of motion of a caravan of camels or buses is determined by the slowest member.

The reaction between H_2 and I_2 to give HI is typical of reactions which take place in a single step. This is consistent with the rate equation and the overall reaction.

$$\text{RATE} = k[H_2][I_2]$$

However, the simple overall reaction between H_2 and Br_2 to give HBr involves several steps as shown in section 13.1.5. Let us consider the decomposition of N_2O_5 which shows first-order behaviour:
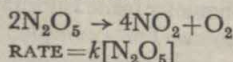
$$2N_2O_5 \rightarrow 4NO_2 + O_2$$
$$\text{RATE} = k[N_2O_5]$$

This reaction, although the overall order is one with respect to N_2O_5, involves several steps as shown below:

$$N_2O_5 \rightarrow NO_2 + NO_3$$
$$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$$
$$NO + NO_3 \rightarrow 2NO_2$$
$$NO_2 + NO_3^- \rightarrow N_2O_5$$
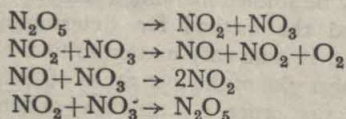
Each of these steps is called an *elementary process* and the collection of such elementary processes giving the overall reaction is called a *reaction mechanism*. We can rightaway see that the overall order of the reaction does not say any-

thing about the various steps or the mechanisms. We shall show later how the dissociation of N_2O_5 works out to be first order in spite of so many steps in the reaction.

13.3.1 Molecularity and Elementary Processes

Each elementary process in a many-step reaction mechanism, can be individual-ly characterised in terms of the number of molecules involved or its *molecularity*. For example, a *unimolecular process* is one where only a single molecule is involved in a rearrangement or a fragmentation reaction. The following are typical uni-molecular processes:

$$O_3 \rightarrow O_2 + O$$
$$H_3C{-}CH_3 \rightarrow 2CH_3$$
$$H{-}Cl \rightarrow H + Cl$$
$$N_2O_5 \rightarrow NO_2 + NO_3$$
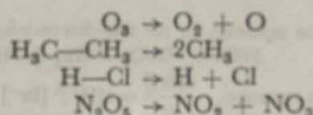
Bimolecular processes involve two reacting species:

$$CH_4 + Cl \rightarrow CH_3 + HCl$$
$$NO + NO_3 \rightarrow 2NO_2$$
$$C_2H_6 + CH^+_4 \rightarrow C_2H_5 + CH^+_5$$
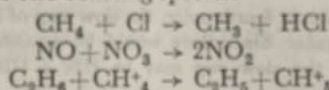
Termolecular processes involve three species and are not too common:

$$2NO + Br_2 \rightarrow 2NOBr$$
$$NO + N_2 + O \rightarrow NO_2 + N_2$$
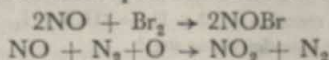
Processes where more than three species are involved are rarer.

We had mentioned earlier in the chapter that the order of a reaction cannot be predicted from the stoichiometry of a reaction. However, in the case of *elementary processes, order and molecularity are identical*. Thus, a unimolecular elementary process is a first-order reaction while a bimolecular elementary process is a second-order reaction. We emphasise once again that the order of a reaction does not directly reflect the molecularity; a first-order reaction need not be unimolecular. For example the first-order decomposition of N_2O_5 actually involves unimolecular as well as bimolecular elementary processes. From this discussion it becomes evident that we can correctly relate the order and stoichiometry (or molecularity), only in the case of an elementary process. We shall now examine how to relate the experimentally observed rate and order of an overall reaction to the rates and orders of elementary processes responsible for the mechanism.

13.3.2 Rate Laws and Mechanisms

Let us consider the overall general reaction,
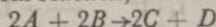
$$2A + 2B \rightarrow 2C + D$$

This reaction may actually proceed by following four elementary steps:

$$
\begin{array}{ll}
A + B \rightarrow E + F & \text{(BIMOLECULAR)} \\
B + F \rightarrow P & \text{(BIMOLECULAR)} \\
E \rightarrow Q & \text{(MONOMOLECULAR)} \\
\underline{P + Q + A \rightarrow 2C + D} & \text{(TERMOLECULAR)} \\
\end{array}
$$
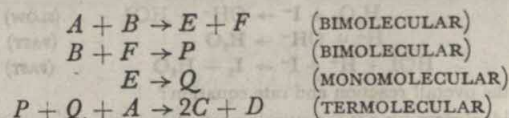
Adding, $\quad \overline{2A + 2B \rightarrow 2C + D}$

The products C and D can only be formed as fast as the slowest step or the *rate-determining step* in the reaction. If the first step (bimolecular reaction) is the

30

slowest step, the reaction will be second order. We, thus, see that a reaction following a simple rate law can actually have a complicated mechanism.

In many simple reactions, the rate-determining step is the very first step which is then followed by rapid subsequent reactions as exemplified by the reaction between NO_2 and F_2 to give NO_2F.
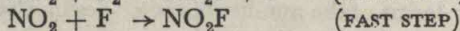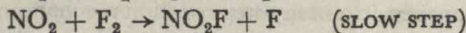
$$NO_2 + F_2 \rightarrow NO_2F + F \quad \text{(SLOW STEP)}$$
$$NO_2 + F \rightarrow NO_2F \quad \text{(FAST STEP)}$$
$$\text{RATE} = k[NO_2][F_2]$$

This mechanism is consistent with the observed second-order of the reaction.

Example 13.9 Suggest an equation for the rate-determining step for the overall reaction,
$$5HBr + HBrO_3 \rightarrow 3Br_2 + 3H_2O$$
given the differential rate equation, $\dfrac{d[Br_2]}{dt} = k[H^+]^2[Br^-][BrO^-_3]$
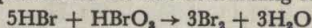
Although the rate equation is fourth order, the slow step of importance to the mechanism is *most likely* to be bimolecular. Since there would be equilibria such as, $H^+ + Br^- \rightleftharpoons HBr$, $H^+ + BrO^-_3 \rightleftharpoons HBrO_3$, the slow step may be $HBr + HBrO_3 \rightarrow$ products. Further steps would be fast.

Example 13.10 For the reaction $2ICl + H_2 \rightarrow 2HCl + I_2$, the rate has the form: rate $= k[ICl][H_2]$. What is the rate-determining step?

The rate-determining step in this mechanism is a slow bimolecular reaction between ICl and H_2. The kinetic data on this system has indeed been explained in terms of a two-step mechanism:

$$ICl + H_2 \xrightarrow{\text{slow}} HI + HCl \quad \text{(RATE-DETERMINING STEP)}$$
$$ICl + HI \xrightarrow{\text{fast}} HCl + I_2 \quad \text{(FAST STEP)}$$
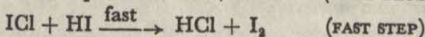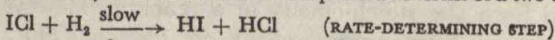
Example 13.11 For the reaction, $3I^- + S_2O^{2-}_8 \rightarrow 2SO^{2-}_4 + I^-_3$, the differential rate expression is given by:

$$\text{RATE} = \frac{d[I^-_3]}{dt} = k[I^-][S_2O^{2-}_8]$$

What is the rate-determining step?

The rate-determining step could be the slow reaction between the ions of the same charge,

$$I^- + S_2O_8^{2-} \xrightarrow{\text{slow}} [IS_2O_8]^{3-}$$
$$(IS_2O_8)^{3-} \xrightarrow{\text{fast}} I^+ + 2SO_4^{2-}$$
$$I^+ + I^- \xrightarrow{\text{fast}} I_2$$
$$I_2 + I^- \xrightarrow{\text{fast}} I_3^-$$
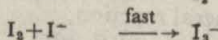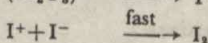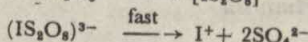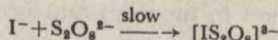
Example 13.12 The mechanism for the oxidation of iodide ion by H_2O_2 in acid medium has been suggested to be the following:

$$H_2O_2 + I^- \rightarrow OH^- + HOI \quad \text{(SLOW)}$$
$$H^+ + OH^- \rightarrow H_2O \quad \text{(FAST)}$$
$$HOI + H^+ + I^- \rightarrow I_2 + H_2O \quad \text{(FAST)}$$
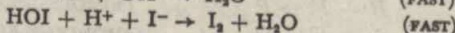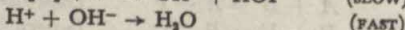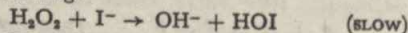
What should be the overall reaction and rate equation?
Adding the individual steps we get the overall reaction to be
$$H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$$
Since the slowest step determines the rate,
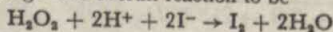
$$\text{RATE} = \frac{-d[H_2O_2]}{dt} = k[H_2O_2][I^-]$$

There are some reactions where the first step involves a rapid equilibrium which produces an intermediate which then reacts slowly in the rate-determining step. An example of such a reaction is the reaction of NO and O_2 to produce NO_2.

$$2NO + O_2 \rightarrow 2 NO_2$$
$$\text{RATE} = k\,[NO]^2\,[O_2]$$
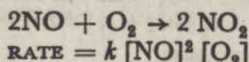
The observed rate law shows that the reaction is second order with respect to NO and first order with respect to O_2. One *possible mechanism* that is consistent with the rate law is the following:

$$NO + NO \rightleftharpoons N_2O_2 \quad (\text{FAST})$$
$$N_2O_2 + O_2 \rightarrow 2NO_2 \quad (\text{SLOW})$$
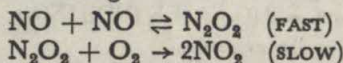
The first step involves an equilibrium and we can write the equilibrium expression.

$$K = [N_2O_2]/[NO]^2 \quad \text{or,} \quad [N_2O_2] = K\,[NO]^2$$

The rate of the slow step is given by,

$$\text{RATE} = k'\,[N_2O_2]\,[O_2] = k'\,K[NO]^2\,[O_2] = k\,[NO]^2\,[O_2]$$

13.3.3 Steady State Approximation

Till now we have considered reactions where one of the steps is slow and rate-determining. There are reactions, however, where several or all the steps in the mechanism are relatively slow or of similar rates. In order to derive the rate law for such reactions, we make use of the *steady-state approximation*. In this situation, a reaction intermediate is produced by a previous step, and is lost in a following reaction. Under conditions when the rates of the two steps match, the concentration of the intermediate does not undergo any net change. This is somewhat akin to the case of the much desired state of 'zero population growth' in the world, where the birth rate and death rate equal one another, leading to a constant population level. This conceptual basis of the steady-state approximation is shown in Fig. 13.5.

Fig. 13.5 The steady state approximation. The concentrations of reactant (R) and product (P) change appreciably with time, but that of the reaction intermediate (I) starts from zero, remains steady for an appreciable time shown by the broken lines, and goes down to zero at the end of the reaction.
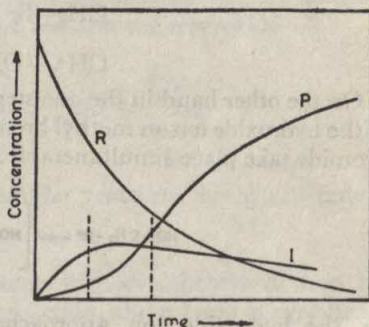
As an illustrative example of this approximation, let us examine the first-order decomposition of N_2O_5:

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$
$$\text{RATE} = k\,[N_2O_5]$$
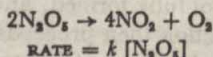
Earlier in this section (see page 440), we showed the three elementary processes involved in the mechanism of this decomposition reaction. We see that NO_3 and NO are the two intermediates in the reaction. Applying the steady state approximation,

$$\text{RATE OF DESTRUCTION OF NO} = \text{RATE OF FORMATION OF NO}$$
$$k_3\,[NO]\,[NO_3] = k_2\,[NO_2]\,[NO_3]$$

where k_2 and k_3 are the rate constants for steps two and three respectively. We, therefore, have

$$[NO] = (k_2/k_3)\ [NO_2]$$

Similarly, for NO_3,

RATE OF DESTRUCTION OF NO_3 = RATE OF FORMATION OF NO_3

$$[NO_3]\ \{k_2\ [NO_2] + k_3\ [NO] + k_4\ [NO_2]\} = k_1\ [N_2O_5]$$

Substituting for [NO] by the earlier expression,

$$[NO_3] = \frac{k_1\ [N_2O_5]}{k_4\ [NO_2] + 2k_2\ [NO_2]}$$

The rate of formation of $[O_2]$ is given by

$$RATE = d\ [O_2]/dt = k_2\ [NO_2]\ [NO_3]$$

Substituting for $[NO_3]$ by the earlier expression,

$$\frac{d\ [O_2]}{dt} = \frac{k_1 k_2\ [N_2O_5]}{k_4 + 2k_2}$$

$$RATE = k\ [N_2O_5]$$

We see that the rate constant k actually involves rate constants of the individual elementary processes.

13.4 CASE STUDIES IN REACTION MECHANISMS

Case 1: Consider a substitution reaction like the reaction between methyl bromide and hydroxide ion which yields methanol.

$$CH_3-Br + NaOH \rightarrow CH_3-OH + NaBr$$
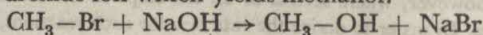
There are two distinct mechanistic possibilities for this reaction: (1) a two-step mechanism, and (2) a one-step mechanism. In the two-step mechanism (1), the initial step is assumed to be a slow reversible dissociation of the carbon-bromine bond of methyl bromide giving methyl *carbonium ion*, CH_3^+ and bromide ion. The second step involves a fast reaction between the methyl carbonium ion, and the hydroxide ion to give methanol.

$$\left.\begin{array}{l} CH_3-Br \overset{slow}{\underset{fast}{\rightleftharpoons}} CH^+_3 + Br^- \\ CH^+_3 + OH^- \rightarrow CH_3-OH \end{array}\right\} \quad\quad (1)$$
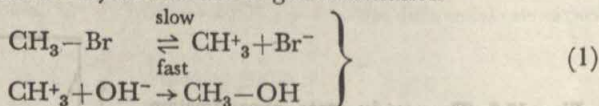
On the other hand in the one-step process (2), it is postulated that the attack of the hydroxide ion on methyl bromide and the loss of bromide ion from methyl bromide take place simultaneously:

$$HO + CH_3-Br \rightarrow \left[HO - \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}} \overset{H}{-} Br \right] \rightarrow CH_3-OH + Br \quad\quad (2)$$
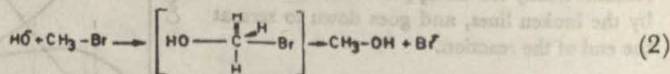
As the hydroxide ion approaches methyl bromide, O—C bond will be gradually formed and simultaneously the C—Br bond in methyl bromide will become weaker. As this process continues, a transition state is reached in which O—C bond is partly, but not fully formed, and the C—Br bond is partly, but not fully, broken. The reaction then proceeds further to give methanol with the loss of bromide ion (for details, see Chapter 14).

How do we decide as to which one of these mechanisms is actually applicable to the case of the reaction of hydroxide ion with methyl bromide? One way of finding out is to study the rate of this chemical reaction. On examination of the two-step mechanism, it becomes clear that the rate-determining step (slowest step in the two-step process) is the dissociation of methyl bromide to give methyl

carbonium ion and bromide ion. The rate of reaction of hydroxide ion with methyl bromide should therefore be dependent only on the concentration of methyl bromide and not on hydroxide ion concentration. The hydroxide ion is consumed only in a fast secondary reaction. Experimental studies have shown that the rate of the reaction of methyl bromide depends on the concentration of both reactants, methyl bromide and hydroxide ion. The reaction is first-order both with respect to CH_3Br and OH^-. This is indicated by the following expression:

$$\text{RATE} = k\,[CH_3\text{—}Br][OH^-]$$

We can now safely conclude on the basis of the kinetic results that the two-step mechanism (1) involving the formation of methyl carbonium ion is not applicable to the reaction of methyl bromide. On the other hand, the kinetic results are in agreement with the one-step mechanism (2) in which we assume that the rate-determining step of the reaction (leading to the formation of the transition state) involves the collision between a hydroxide ion and a methyl bromide molecule.

However, a substitution reaction like the reaction between *t*-butyl bromide and hydroxide ion to give *t*-butyl alcohol proceeds by a two-step mechanism. Here, the rate of reaction depends only on the concentration of *t*-butyl bromide and not on hydroxide ion concentration:

$$\text{Rate} = k\,[(CH_3)_3\,CBr]$$
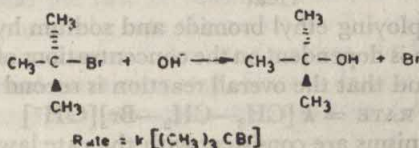
The two steps of this reaction include the initial slow ionisation of *t*-butyl bromide to give the *t*-butyl carbonium ion and the bromide ion, followed by a fast reaction between the *t*-butyl carbonium ion and the hydroxide ion.
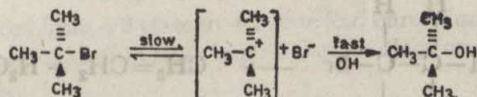
Thus, we see that the kinetic schemes for similar reactions being different for different reactant molecules.

Case 2: It is well known that bromine reacts with cyclohexene to form 1, 2-dibromocyclohexane. During this addition reaction, the π bond of cyclohexane is broken and two new σ-bonds are formed.
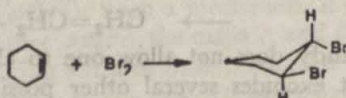
Experimental studies indicate that the reaction follows second-order kinetics, and the configuration of the dibromo compounds is *trans*.

$$\text{RATE} = k\,[\text{cyclohexene}][Br_2]$$

This would be consistent with either a one-step bimolecular reaction mechanism (1), or a two-step mechanism (2):
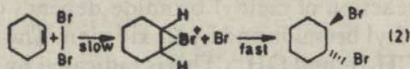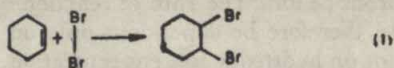
A one-step reaction (1) should lead to *cis*-1, 2 dibromocyclohexane. Mechanism (2) proposes that the olefin is attacked by bromine to give the intermediate, cyclic·bromonium ion, in the slow-step process. This is followed by a fast attack of bromide ion on the intermediate to give *trans*-1, 2-dibromocyclohexane. Thus, the possible mechanism (1), although in agreement with the reaction kinetics, has been excluded.

Case 3: Ethyl bromide, on heating with a strong base like sodium hydroxide, gives ethylene with the elimination of the elements of hydrogen bromide (dehydrohalogenation). In the overall reaction, two bonds are broken (C—H and C—Br) and a new C—C bond is formed:

$$CH_3-CH_2-Br \xrightarrow[\text{Heat}]{\text{NaOH}} CH_2=CH_2 + H_2O + NaBr$$
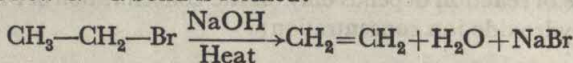
Kinetic studies employing ethyl bromide and sodium hydroxide reveal that the rate of elimination is dependent on the concentrations of both ethyl bromide and hydroxide ion, and that the overall reaction is second order.

$$\text{RATE} = k\,[CH_3-CH_2-Br][OH^-]$$

Two simple mechanisms are consistent with the rate law. In the first, a one-step mechanism (1), the base removes the β-hydrogen while the leaving-group leaves from the α-carbon. In the second, the base removes the β-hydrogen to form a carbanion (see section 14.2.3) which subsequently loses the bromide ion to make ethylene.

$$\begin{array}{ccc} & H \ \ H & \\ & | \ \ \ | & \\ HO^- + H-C-C-Br & \longrightarrow & CH_2=CH_2 + H_2O + Br^- \quad (1) \\ & | \ \ \ | & \\ & H \ \ H & \end{array}$$

$$\begin{array}{ccc} & H \ \ H & \\ & | \ \ \ | & \quad \text{slow} \\ HO^- + H-C-C-Br & \longrightarrow & {}^-CH_2-CH_2-Br + H_2O \\ & | \ \ \ | & \\ & H \ \ H & \end{array}$$

$$\text{fast} \longrightarrow CH_2=CH_2 + Br^- \quad (2)$$
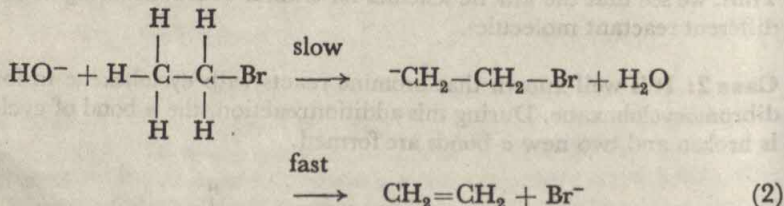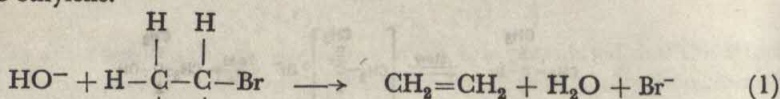
Although a kinetic study does not allow one to choose between the two possible mechanisms, it excludes several other possible mechanisms. Since there is experimental evidence that a measurable amount of carbanion is not formed during such elimination reactions, it has been concluded that a one-step mechanism (1) explains the reaction.

Case 4: Let us consider the reaction,

$$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^-$$
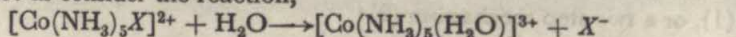
where X is an anion like Cl^-. For such a reaction, the experimentally observed rate law is,

$$\text{RATE} = k\left\{[Co(NH_3)_5 X]^{2+}\right\}$$

The rate is determined only by the concentration of the complex ion, suggesting a dissociative type of mechanism. However, this reaction has been carried out in aqueous medium where the concentration of H_2O is essentially constant. Because of this, the rate law given by the above equation cannot be experimentally distinguished from the rate law,

$$\text{RATE} = k'\,[H_2O]\,\left\{[Co(NH_3)_5 X]^{2+}\right\}$$

$k = k'[H_2O]$. That is, the rate law does not tell us if H_2O is also involved in the rate-determining step. Obviously, other experimental data are needed to decide between the two mechanisms.

One of the several experiments which can be carried out in order to distinguish between these two mechanisms is the effect of charge of the reacting complex ion species on the rate of reaction. It has been observed that the rate of hydrolysis of *trans*-$[Co(NH_3)_4Cl_2]^+$ is approximately 10^3 times faster than that of $[Co(NH_3)_5Cl]^{2+}$. One can expect that the increased charge on the complex-ion will attract the incoming ligand and will increase the rate of reaction. At the same time, increased charge will retard the metal-ligand bond cleavage, and decrease the rate of reaction. Thus, if the effect of increased charge is not significant on the rate of reaction, both bond-breaking and bond-forming are important, whereas if the rate decreases, the bond formation is not important in the rate-determining step. Since a decrease in rate (10^3 times) is observed as the charge on the complex increases from $+1$ to $+2$, a dissociative path seems likely.

Case 5 : In the redox reaction,

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} + 5H_2O \rightarrow$$
$$[Co(H_2O)_6]^{2+} + [Cr(H_2O)_5Cl]^{2+} + 5NH_3$$
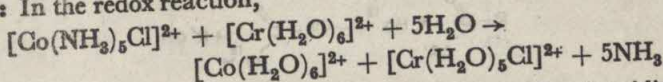
cobalt ion is reduced from $+3$ state to $+2$ state and chromium is oxidised to $+3$ state. This change in oxidation state implies that an electron is transferred from Cr(II) to Co(III).

$$Cr(II) \rightarrow Cr(III) + e^-$$
$$Co(III) + e^- \rightarrow Co(II)$$
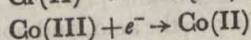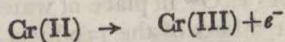
The reaction proceeds according to the rate law,

$$\text{RATE} = k\left\{[Co(NH_3)_5Cl]^{2+}\right\}\left\{[Cr(H_2O)_6]^{2+}\right\}$$

The transfer of electron in this reaction can take place in one of two possible ways. In one the Cr (II) and Co(III) ions come close together and the electron jumps from Cr(II) to Co(III). Such a mechanism is called the *electron transfer mechanism*. In the other mechanism, the oxidant and the reductant are bonded to each other by a bridging atom or molecule and through which an electron passes. The bridging atom in such a case acts like a conducting wire connecting the two electrodes. Such a mechanism is called *atom transfer mechanism*. It is observed that in the reduction of $[Co(NH_3)_5Cl]^{2+}$ by $[Cr(H_2O)_6]^{2+}$, the chromium (III) product always contains a chloride ion. It has been shown by using radioactive chlorine that Cl^- ion is transferred from the Co^{3+} complex.

To explain these results a complex molecule is postulated in which chloride

of the Co(III) complex acts as a bridge between Cr(II) and Co(III) (through which the electron passes). Once the electron is transferred, Cr(III) attracts chlorine more strongly than Co(II) and, therefore, the chloride ion becomes part of the Cr(III) complex.

The postulated reaction mechanism is as follows:

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [(NH_3)_5\!-\!Co\!-\!Cl\!-\!Cr(H_2O)_5]^{4+} + H_2O$$

$$[(NH_3)_5Co\!-\!Cl\!-\!Cr(H_2O)_5]^{4+} + nH_2O + 5H^+ \overset{k_3}{\longrightarrow} [CO(H_2O)_6]^{2+} +$$
$$[Cr(H_2O)_5Cl]^{2+} + 5NH^+_4$$
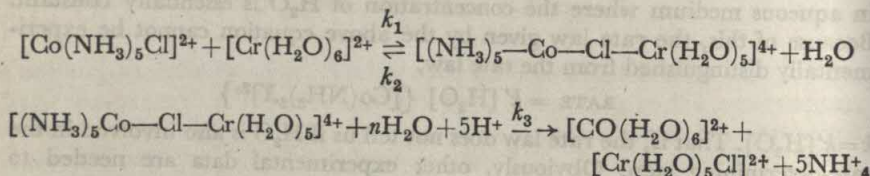
Many other reduction experiments of Co (III) complexes, $[Co(NH_3)_5X]^{2+}$ with $[Cr(H_2O)_6]^{2+}$ have been studied. It has been shown that even when X is NCS^-, N^-_3, PO^{3-}_4, Cl^-, Br^- or SO^{2-}_4, the transfer of X^- to Cr (II) occurs suggesting the atom transfer mechanism for these reactions.

13.4.1 Use of Isotopes in Mechanistic Studies

In case 5 above, we had mentioned that radioactive chlorine was used to show that a chloride ion is transferred from the Co^{3+} complex. Use was made of the fact that it is possible to 'tag' the chlorine by a label that is radioactive, in this case. The utility of isotopes in diagnosing mechanistic pathways arises from the fact that isotopes of a given atom, while chemically identical, possess different masses, and in many cases different magnetic properties, radioactive and so on. An interesting example of the use of isotopes in the study of reactions occurs in the case of ester hydrolysis.

$$R\!-\!\overset{\displaystyle O}{\underset{\displaystyle OR'}{\overset{\|}{C}}} + HO^{18}H \longrightarrow R\!-\!\overset{\displaystyle O}{\underset{\displaystyle O^{18}H}{\overset{\|}{C}}} + R'OH$$
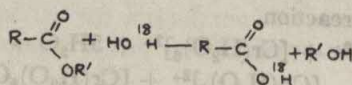
In this reaction, the hydrolysis can happen either by breaking the C—O bond and adding OH from water, or by breaking the O—R' bond and adding a H from water. When one uses H_2O^{18} in place of water in the above reaction, and determines the molecular masses of the products by mass spectrometry, one finds that the O^{18} is incorporated in the acid, and not in the R'OH, showing thereby that the C—O bond in the ester is ruptured during hydrolysis.

If we study the decomposition of N_2O, using N^{15}, the mechanism

$$N^{15}N^{14}O \rightarrow N^{15} + N^{14}O$$
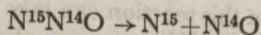
will give rise to $2N^{15} \rightarrow N^{15} \equiv N^{15}$ or nitrogen that has a molecular mass of 30, while the mechanism

$$N^{15}N^{14}O \rightarrow {}^{15}N\ N^{14} + O$$
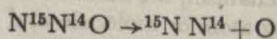
will give nitrogen gas of molecular mass 29. Analysis of products by mass spectrometry supports the former mechanism.

Use can also be made of the fact that some isotopes of a given atom, while chemically identical, possess radioactivity (see Chapter 19). The radioactivity can be monitored by instruments called Geiger counters.

In some cases, different reaction rates for compounds found with different

isotopes may be advantageously used to elucidate the reaction mechanism. Such *kinetic isotope effects*, however, are not significant when the atomic mass of the isotope is high. With hydrogen and deuterium, where the ratio of masses of the two isotopes is high (mass of deuterium/mass of hydrogen$=2$), the isotope effect becomes significant. Any chemical bond with deuterium has a higher bond energy compared to a similar one with hydrogen and consequently those reactions which involve a bond rupture with hydrogen will take place with a slower rate if the hydrogen is replaced by deuterium. Thus, if one has to find out the importance of a bond rupture involving hydrogen in the overall reaction, a study of the deuterium isotope effect often helps. For example, it is now established that in the oxidation of *iso*-propanol to acetone using dichromate in acidic solution,

$$\begin{array}{ccc}
\text{H} & \text{OH} & \text{H} \\
| & | & | \\
\text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\
| & | & | \\
\text{H} & \text{H} & \text{H}
\end{array}
\rightarrow
\begin{array}{ccc}
\text{H} & \text{O} & \text{H} \\
| & \| & | \\
\text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\
| & & | \\
\text{H} & & \text{H}
\end{array}$$

<center>iso-propanol   acetone</center>
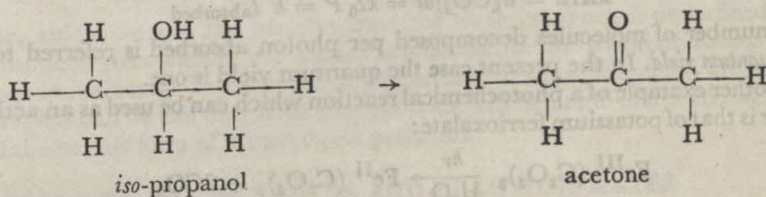
the C—H bond rupture of the central carbon atom comprises the rate-determining step. This was found by taking partially deuterated *iso*-propanol with deuterium instead of hydrogen on the central carbon atom and studying its rate of oxidation. It was found out that the reaction

$$\begin{array}{ccc}
\text{H} & \text{OH} & \text{H} \\
| & | & | \\
\text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\
| & | & | \\
\text{H} & \text{D} & \text{H}
\end{array}
\rightarrow
\begin{array}{ccc}
\text{H} & \text{O} & \text{H} \\
| & \| & | \\
\text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\
| & & | \\
\text{H} & & \text{H}
\end{array}$$
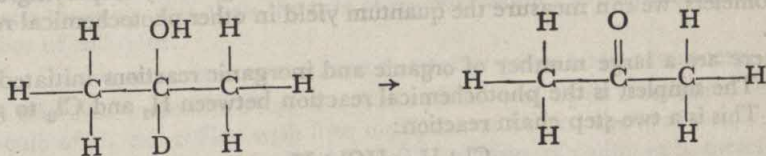
was about six times slower than the corresponding undeuterated compound. This means that C—D bond rupture is one of the rate-determining steps; if it were not, the rate of oxidation would have remained unaffected.

13.5 PHOTOCHEMICAL REACTIONS

Instead of heat, photons are often employed to energise chemical reactions. Usually radiation of well-defined energy is employed for this purpose. The energy or the frequency of radiation depends on the strength of the bond that needs to be broken in the reaction. For example, for the dissociation of iodine,

$$I_2 + h\nu \rightarrow 2\ I$$
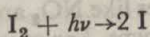
the longest wavelength of radiation that one can employ is 7950 A since the bond energy of iodine is 36 kcal mol^{-1}.

Rates of photochemical reactions depend on the intensity of the radiation (remember that the number of photons is related to intensity). An important feature of a photochemical experiment is the measurement of the intensity of radiation. The unit of photochemical intensity is an Einstein (which is equal to the energy of one mole of photons, $N h\nu$) per second. The intensity is generally measured by employing an *actinometer*, which is a chemical system whose photo-

chemical behaviour is quantitatively known. One such actinometer is the photochemical decomposition of acetone:

$$CH_3COCH_3 + h\nu \rightarrow CH_3{\cdot} + CH_3CO{\cdot}$$
$$CH_3CO{\cdot} \rightarrow CH_3{\cdot} + CO$$
$$CH_3{\cdot} + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2{\cdot}$$
$$CH_3{\cdot} + CH_3COCH_2{\cdot} \rightarrow CH_3COCH_2CH_3$$
$$2CH_3{\cdot} \rightarrow C_2H_6$$
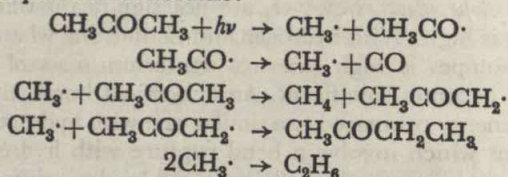
Since one molecule of CO is produced for each photon absorbed, a measurement of the amount of CO at any time can be readily related to the intensity of the source (used for radiation), I_0, if the fraction of incident light absorbed is known:

$$\text{RATE} = d[CO]/dt = kI_0 P = k' I_{absorbed}$$

The number of molecules decomposed per photon absorbed is referred to as the *quantum yield*. In the present case the quantum yield is one.

Another example of a photochemical reaction which can be used as an actinometer is that of potassium ferrioxalate:

$$Fe^{III} (C_2O_4)_3 \xrightarrow[H_2O]{h\nu} Fe^{II} (C_2O_4)_2 + 2CO_2$$
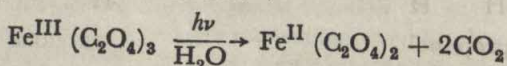
where ferric iron is converted into ferrous iron and carbon dioxide is evolved. In this case, the quantum yield is near unity and the products do not absorb the incident radiation during photolysis. The ferrioxalate system is a sensitive actinometer and can be used in the 2540–5780 A region. By employing such actinometers, we can measure the quantum yield in other photochemical reactions.

There are a large number of organic and inorganic reactions initiated by light. The simplest is the photochemical reaction between H_2 and Cl_2 to give HCl. This is a two-step chain reaction:

$$Cl + H_2 \rightarrow HCl + H$$
$$H + Cl_2 \rightarrow HCl + Cl$$
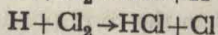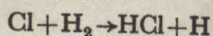
The chlorine atoms are produced photochemically, by focussing blue light on the reaction flask.

$$Cl_2 + h\nu \rightarrow Cl_2{}^* \rightarrow 2\,Cl$$
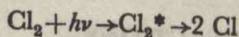
Some organic reactions induced by light are discussed in Chapter 15.

13.6 ATMOSPHERIC POLLUTION AND FORMATION OF SMOG

Exhaustive studies have been carried out on the kinetics of atmospheric *pollution* and the consequent formation of *smog*. Gases like NO_2 and SO_2 are found in the atmosphere of most cities and industrial towns. For example, NO_2 is produced by the oxidation of NO which in turn is formed by the combination of N_2 and O_2 in various combustion reactions. SO_2 and SO_3 are formed by the combustion of coal and oil. Molecules of NO_2 and SO_2 can absorb light energy and produce reactive atoms or radicals:

$$NO_2 + h\nu \rightarrow NO + O$$
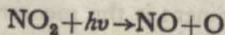
Hydrocarbons (from spilled or partially burnt fuel from automobiles, industries or homes) react with oxygen atoms to produce aldehydes and hydrocarbon

free radicals; the latter react with O_2 and NO to produce more oxygen atoms and propagate the chain reaction:

$O + HC \rightarrow R \cdot + \underline{RCHO}$ (HC = hydrocarbon; R· = hydrocarbon radical)
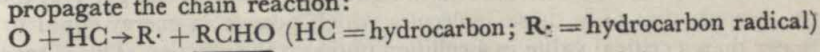
Oxygen atoms also combine with O_2 to produce ozone which in turn can produce aldehydes.

$$O + O_2 \rightarrow \underline{O_3}$$

$$O_2 + HC \rightarrow RCO_2 \cdot + \underline{RCHO}$$

$$RCO_2 \cdot + NO \rightarrow RCO \cdot + NO_2$$

$$RCO + NO_2 + O_2 \rightarrow R \overset{\overset{O}{\|}}{-C} - O - O - NO_2$$
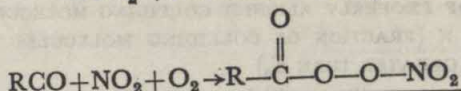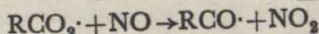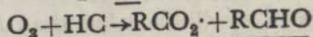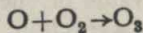
Ozone, aldehydes and the peroxynitrate(the three compounds underlined in the reactions given above) are mainly responsible for the irritation caused by photochemical smog. The kinetics of photochemical smog formation are well-understood and we can only hope that good use will be made of this knowledge to minimise this form of atmospheric pollution.

13.7 MOLECULAR COLLISIONS AND REACTION RATES

Consider a reaction between two molecules A_2 and B_2 :

$$A_2(g) + B_2(g) \rightarrow 2 \, AB(g)$$
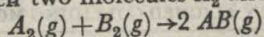
If we postulate that the reaction between A_2 and B_2 proceeds through collisions between the molecules, then the rate of reaction would be proportional to the number of collisions:

RATE $\propto$ NUMBER OF MOLECULES COLLIDING PER LITRE PER SECOND

If we take four molecules of A_2 and four molecules of B_2 in a container, each molecule of A_2 can collide with four molecules of B_2 and the total number of collisions of A_2 with B_2 will be $4 \times 4 = 16$. The number of collisions is, therefore, directly proportional to the product of concentrations of A_2 and B_2:

NUMBER OF COLLISIONS $\propto [A_2][B_2]$

We clearly see how the rate works out to be proportional to the product of concentrations from collision theory.

Not every collision between molecules results in a reaction. If we compare the calculated number of collisions per second with the observed reaction rate, we

Fig. 13.6 Importance of the alignment of molecules in the reaction $2AB \rightarrow A_2 + B_2$. Alignment (a) leads to reaction, while alignment (b) does not.
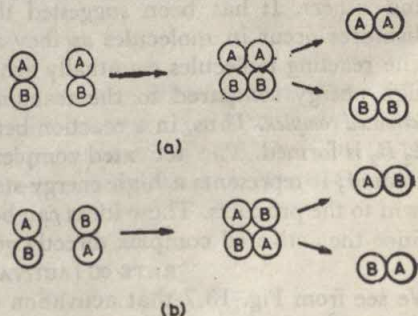
find that only a small fraction of the total number of collisions is effective. There can be two reasons why a collision may not be effective: (i) The molecules

are not properly aligned (Fig. 13.6) and (*ii*) the impact of the collision may be so small that the molecules rebound without any change in energy. We, therefore, propose that only those molecules which possess an energy equal to or greater than a critical value in a collision undergo the reaction. This is reasonable since a molecule like HI can be decomposed ($2HI \rightarrow H_2 + I_2$), only if the H—I bond is weakened. The critical value of energy is referred to as the *activation energy*, E_a, and is characteristic of a reaction. There will be no reaction if the energy of molecules in a collision is less than E_a. We can now write the expression for rate as

RATE $=$ (NUMBER OF PROPERLY ALIGNED COLLIDING MOLECULES PER LITRE PER SECOND) $\times$ (FRACTION OF COLLIDING MOLECULES WITH ENERGY EQUAL TO OR GREATER THAN E_a)

At any given temperature, there will be a distribution of kinetic energies (or velocities) of molecules (see Chapter 6). The energies vary anywhere between zero to some high value. According to the collision theory, only those molecules with energies equal to or greater than E_a will participate in the reaction. The fraction of such molecules can be increased by increasing the temperature. The number of collisions is also increased by temperature, but that will not be very significant. The increase in reaction rate with temperature is, therefore, mainly due to the increased number of energetic molecules. The rate of a reaction may now be expressed as

$$RATE = \frac{\text{NUMBER OF PROPERLY ALIGNED COLLIDING MOLECULES}}{\text{LITRE SECOND}} \; e^{-E_a/RT}$$

$$= (\text{CONSTANT FOR A GIVEN REACTION}) \; e^{-E_a/RT}$$

Here, the factor $e^{-E_a/RT}$ represents the fraction of molecules that have energies equal to or greater than E_a. The *larger* the value of E_a, *smaller* is the fraction of energetic molecules that can participate in the reaction and *slower* is the reaction.

In the above discussion, we have assumed that molecules make use of only kinetic energy to acquire energies of the order of E_a. The kinetic energy is converted into vibrational energy on collision and the molecules vibrate violently. The large amplitudes of vibration loosen the bonds, a condition necessary for the reaction. We must note here that this simple-minded collision theory of reaction rates is not entirely satisfactory. It gives poor agreement with experimental values in many reactions.

The classical collision theory described above has been modified by Eyring and others. It has been suggested that significant changes in interatomic distances occur in molecules as they approach each other during collisions. The reacting molecules eventually achieve a specific configuration possessing high energy compared to the reactants. Such a configuration is called an *activated complex*. Thus, in a reaction between A_2 and B_2, an activated complex $A_2 B_2$ is formed. The activated complex is not a stable species and cannot be isolated; it represents a high energy state through which the reactants transform to the products. These ideas can be pictorially represented as in Fig. 13.7. Since the activated complex directly goes to products,

RATE $\propto$ [ACTIVATED COMPLEX]

We see from Fig. 13.7 that activation energy represents the potential energy barrier the reactants have to cross to transform into the products. The energy of the products is lower than that of the reactants and the difference in energy

Fig. 13.7 Potential energy diagram for the reaction $A_2 + B_2 \rightarrow$ ACTIVATED COMPLEX $\rightarrow$ $2AB$. The potential energy is plotted against the *reaction coordinate*, representing the progress of molecules from the form of reactants to that of products. The changes in bond distances that accompnay this transformation are reflected in the reaction coordinate. The reaction coordinate actually represents the path of the reaction across a potential energy surface.
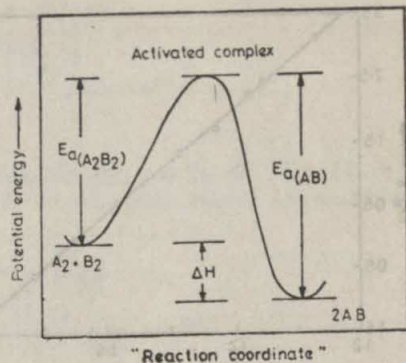
is the thermodynamic ΔE (or ΔH as the case may be) of the reaction. The reaction $A_2 + B_2 \rightarrow 2\,AB$, as shown in Fig. 13.7 is exothermic. The reverse reaction is, however, endothermic and requires a much higher activation energy,

$$E_a \text{ (reverse)} = E_a \text{ (forward)} + \Delta H$$

13.8 TEMPERATURE AND REACTION RATES

The statement that 'reaction rates are affected by temperature' appeals to commonsense. Reactions which are very slow at ordinary temperatures become fast or even explosive at high temperatures. Reactions which are fast at ordinary temperatures are slowed down by lowering the temperature. We ignite fuels to burn them; we cook food, to make it digestible and edible, by heating; we freeze foods in refrigerators to prevent them from spoiling. These are all examples of controlling chemical reactions by a change in the temperature conditions.

Rates of all reactions do not change to the same extent for the same temperature change. As a rough rule, the rate constant is generally doubled by a rise of $10°$ in temperature. For example, the rate constant for the decomposition of HI increases by a factor $1\cdot7$ for each $10°$ rise in temperature.

In the last section we indicated why temperature affects rates and gave the relation,

$$\text{RATE} \propto e^{-E_a/RT}$$

Arrhenius in 1889 gave the general relation between rate constant at temperature as

$$k = A\,e^{-E_a/RT}$$

where A is a constant characteristic of the reaction. This relation is known as the *Arrhenius equation*. The factor A incorporates terms for other factors like frequency of collisions and geometric requirements of collisions. The factor A does not vary significantly with temperature over narrow ranges of temperature and may be taken as constant.

Taking the logarithm of the Arrhenius equation,

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \text{or, } \log k = \log A - \frac{E_a}{2\cdot303\,RT}$$

According to this relation, a plot of $\log k$ against $1/T$ should give a straight line,
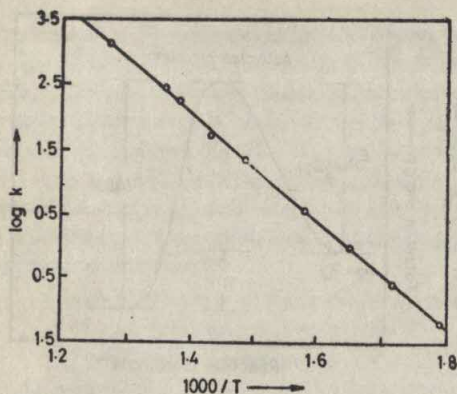
Fig. 13.8 Arrhenius plot of the reaction $H_2 + I_2 \rightarrow 2HI$. The logarithm of the rate constant is plotted against inverse temperature.

which indeed is the case for many reactions (Fig. 13.8). Between any two temperatures, T_1 and T_2, we may write,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2 \cdot 303\, R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where $T_2 > T_1$. The rate constant of a reaction varies markedly with temperature if the value of E_a is high. If the value of E_a is small there will be little change in k with temperature. Activation energies for some gaseous reactions are listed in Table 13.3.

Table 13.3 Activation Energies of Gaseous Reactions

Reaction		E_a, kcal	Reaction		E_a, kcal
$2\,N_2O_5$	$\rightarrow 4NO_2 + O_2$	24·7	$H_2 + I_2$	$\rightarrow 2HI$	40·0
$2\,HI$	$\rightarrow H_2 + I_2$	44·0	$NO + O_3$	$\rightarrow NO_2 + O_2$	2·5
C_2H_5Cl	$\rightarrow C_2H_4 + HCl$	59·0	$H + Br_2$	$\rightarrow HBr + Br$	1·2
$2\,NOCl$	$\rightarrow 2NO + Cl_2$	24·0	$H_2 + Br$	$\rightarrow HBr + H$	17·6

Example 13.13 The complex ion of nickel with ethylene-diamine, $[Ni(en)_3]^{2+}$, dissociates in the presence of strong acid according to the following equation.

$$[Ni(en)_3]^{2+} + 2H_3O^+ \rightarrow [Ni(en)_2(H_2O)_2]^{2+} + [(en)H_2]^{2+}$$
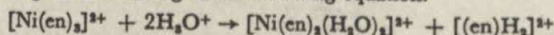
This reaction, which is of first order has a rate constant of 61·4 s^{-1} at 21·8°C and 82·5 s^{-1} at 27·1°C. How do you calculate the activation energy?

$$\log \frac{k_2}{k_1} = \frac{E_a}{2 \cdot 303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$E_a = \frac{2 \cdot 303 \times R \log(k_2/k_1)}{\left(\dfrac{1}{T_1} - \dfrac{1}{T_2} \right)} = \frac{2 \cdot 303 \times 1 \cdot 98 \times \log\left(\dfrac{82 \cdot 5}{61.4} \right)}{\left(\dfrac{1}{273 + 21 \cdot 8} - \dfrac{1}{273 + 27 \cdot 1} \right)} \simeq 18 \text{ kcal}$$

Example 13.14 The activation energy for the transformation of ammonium cyanate to urea has been measured to be 23·2 kcal. The value of A is $4 \cdot 27 \times 10^{13}$ litre mol^{-1} s^{-1}. Calculate the rate constant at 27°C for this reaction.

$$NH_4CNO \rightarrow (NH_2)_2CO$$
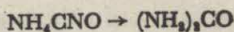
$$k = A e^{-E/RT} = 4.27 \times 10^{12} \left(e^{-\dfrac{23,200}{1.98 \times 300}} \right) \text{litre mol}^{-1} \text{s}^{-1}$$

$$= 4.4 \times 10^{-5} \text{ litre mol}^{-1} \text{s}^{-1}$$

Example 13.15 For the decomposition of N_2O_5 into NO_2 and O_2, the value of E_a is 24.7 kcal. The rate constant at 300 K is 4.0×10^{-5} s^{-1}. What is the value of A in the Arrhenius equation?

$$\log k = \log A - \frac{E_a}{2.303\, RT}$$

$$\log A = \log 4.0 \times 10^{-5} + \frac{24,700}{2.303 \times 1.98 \times 300} = 13.63$$

$$\text{or } A = 4.3 \times 10^{13} \text{ s}^{-1}$$

13.9 CATALYSIS

Rates of reactions can be enhanced to some extent by increasing reactant concentrations and temperature. However, marked changes in rates can be brought about in many reactions by the addition of a substance called a *catalyst*. Catalysts cannot make thermodynamically impossible reactions to occur, but they decrease the activation energies of reactions (the $\Delta H°$ values of the reactions do not change). Catalysts participate in the reaction in one step, but are regenerated again in a later step. The classic example of a catalyst is that of manganese dioxide in the preparation of oxygen by the decomposition of potassium chlorate.

$$2\, KClO_3 \xrightarrow{MnO_2} 2\, KCl + 3\, O_2$$
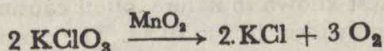
Catalysis can be homogeneous or heterogeneous. In *homogeneous catalysis*, the catalysts and reactants are in the same phase while in *heterogeneous catalysis* the two are in separate phases. We shall now discuss a few examples of catalytic reactions. Just as catalysts accelerate reactions there are also substances which retard reactions; such substances are called *inhibitors* or *negative catalysts*.

Ordinarily, the gas phase reaction of sulphur dioxide with oxygen proceeds slowly:

$$2\, SO_2 + O_2 \rightarrow 2\, SO_3$$
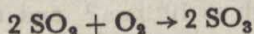
However, the presence of nitric oxide changes the situation completely. Nitric oxide reacts with oxygen through termolecular collisions to form nitrogen dioxide at a reasonable rate. Nitrogen dioxide oxidises sulphur dioxide to sulphur trioxide at a relatively fast pace and regenerates nitric oxide.

$$2\, NO + O_2 \rightarrow 2\, NO_2$$
$$NO_2 + SO_2 \rightarrow NO + SO_3$$
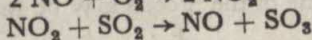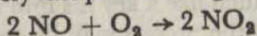
Thus, nitric oxide can be considered to catalyse the formation of sulphur trioxide.

Homogeneous catalysis also occurs in solution phase. There are many reactions catalysed by acids and bases in aqueous media. Decomposition of hydrogen peroxide into water and oxygen is catalysed by iodide ion:

$$H_2O_2\, (aq) + I^-\, (aq) \rightarrow H_2O\, (l) + IO^-\, (aq)$$
$$H_2O_2 + IO^-\, (aq) \rightarrow H_2O\, (l) + O_2\, (g) + I^-\, (aq)$$
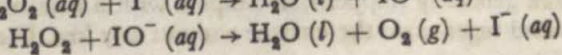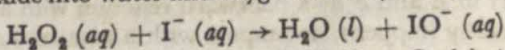
Molecular iodine acts as a catalyst in thermal decomposition reactions of many organic molecules. The iodine molecule, I_2, first dissociates into two iodine atoms which attack organic molecules to initiate chain reactions involving free radicals. The iodine molecule is regenerated later in the reaction.

13.9.1 Enzyme Catalysis

Many chemical reactions that occur inside living systems, termed *biochemical reactions*, often proceed with great speed and efficiency. For a living cell to function, many specific, sequential, and complex reactions have to take place in a programmed manner in the cell. Many of these reactions proceed with slow rates and high activation energies under laboratory conditions and yet in the cell they are carried out with the utmost ease and rapidity. For example, starch (in the form of rice or bread) that we eat as food, gets broken down in the body cells, in a series of about twenty steps, into carbon dioxide and water.

$$\text{STARCH} \rightarrow C_6H_{12}O_6 \text{ (GLUCOSE)}$$
$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O \quad (\Delta H^\circ = -690 \text{ kcal mol}^{-1})$$
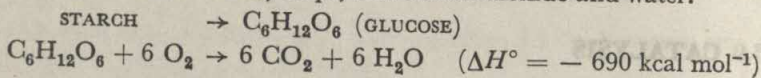
The total time taken for this reaction, termed *oxidative metabolism*, is far less than an hour in the cell. In fact, many cells such as those in bacteria, not only carry out all the reactions necessary for function, but actually duplicate and reproduce themselves within 30 minutes! If we were to attempt all these reactions in the laboratory with the same materials and with such efficiency and yield, it would take months.

In order to carry out all these reactions optimally with speed and efficiency, the cell uses a class of *protein molecules* called *enzymes*, as catalysts, (see Chapter 18 for more details on enzymes). The catalytic efficiency of an enzyme is perhaps the greatest known in nature, often causing biological reactions to proceed to completion within 10^{-3} to 10^{-6} s. The enzyme does this in much the same way as any other catalyst does, that is, by reducing the energy of activation of a given reaction. For example, the activation energy for the decomposition of hydrogen peroxide is reduced from 18,000 cal mol^{-1} to 12,000 cal/mol^{-1} by the use of a platinum catalyst; in the presence of the enzyme catalyst, the activation energy is only 5500 cal mol^{-1}.

Enzyme catalysed reactions are highly specific. A given enzyme performs a particular type of reaction on a given substrate only. The rates of catalysed reactions are often as high as 10^6 min^{-1}, and the catalysis is dependent on conditions like temperature, solvent and pH. All these facts are rationalised in the concept of ' *lock-key* ' *fit theory* of enzyme action (see Chapter 18 for details). The three-dimensional structure of the protein molecule that acts as an enzyme is visualised to possess a specific geometry and the substrate is accommodated in this geometric cavity much like a key fits into a lock.

The reaction scheme of the process may be written as

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \overset{k_3}{\rightarrow} E + P$$
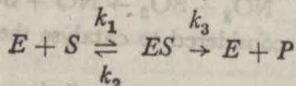
where E is the enzyme, S the substrate and P the product. The enzyme binds the substrate with a rate constant k_1 to produce the complex. The complex may either revert to E and S by a backward reaction with a rate constant k_2, or, as more generally happens, decompose with a rate constant k_3 to produce products and regenerate the enzyme without any loss. Usually, the amount of

Fig. 13.9 Dependence of the velocity of an enzyme-catalysed reaction on the concentration of the substrate (reactant molecule). V_m is the maximum velocity and K_m, the so-called *Michaelis-Menten constant*, is an indication of the efficiency of the enzyme catalyst.
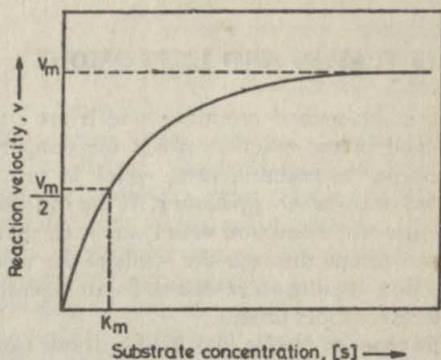
the enzyme catalyst taken in the reaction is much smaller than that of the substrate. Thus, all the enzyme will be bound, or 'saturated', to produce the complex *ES*. Adding any more substrate at this point will not affect the rate. The production of the product is given by the rate $k_3(ES)$, and thus will depend essentially on the complex only. When all the enzyme is saturated, the formation of products will occur at a maximal rate. A plot of the reaction rate against the substrate concentration will look as in Fig. 13.9. The concentration corresponding to $V_m/2 = K_m$ gives an idea of the strength of binding and saturation of the enzyme and the substrate.

One may reduce the efficiency of an enzyme catalysed reaction by using molecules (called *inhibitors*) that are similar to in shape to the substrate molecules. In this situation, the enzyme may be occupied by either the substrate or the inhibitor. The inhibitor reduces the rate of conversion of the substrate by competing for the enzyme site. Also any factors that change the shape of the enzyme molecule will affect the lock-key fit and, thus, the catalytic rate. This is the reason why change of temperature, pH and solvent inactivate enzyme catalysis.

13.9.2 Heterogeneous Catalysis
The use of iron catalyst in the Haber process for the synthesis of ammonia is familiar to us.

$$2\ N_2(g) + 3\ H_2(g) \xrightarrow{\text{Fe}} 2\ NH_3\ (g)$$
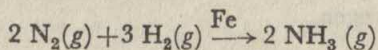
In heterogeneous catalysis, the reactant molecules are held by the surface of the catalyst by fairly strong bonds comparable to chemical bonds (*chemisorption*) and these chemisorbed molecules then proceed to give the products. In some instances, bonds are broken during chemisorption;[*] thus, hydrogen is absorbed in 'atomic' form on metal surfaces like platinum.

There are many heterogeneous catalytic reactions of industrial importance. The *Fischer-Tropsch synthesis* of petrol (gasoline) starting from carbon monoxide and hydrogen is an important example (see Chapter 15). Methanol is produced by the reaction of carbon monoxide and hydrogen over ZnO-Cr_2O_3 catalyst:

$$CO(g) + 2\ H_2(g) \rightarrow CH_3OH(g)$$
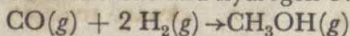
[*]In contrast to chemisorption, molecules are held by weak van der Waals forces in *physical adsorption*, the adsorption of gases on charcoal being a typical example.

Sulphur dioxide is oxidised to sulphur trioxide over platinum catalyst.

$$2 SO_2(g) + O_2(g) \rightarrow 2 SO_3(g)$$
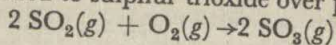
13.10 FLAMES AND EXPLOSIONS

There are several reactions which are sufficiently exothermic and the heat evolved in the reaction raises the temperature of the reaction mixture and increases the reaction rate, which in turn liberates more heat. This effect is called *autocatalytic self-heating.* If the conditions (pressure, temperature and the volume of the reaction vessel) are such that heat is generated much faster than it can escape through the walls of the vessel, then there will be a very rapid reaction causing an *explosion.* In an explosion, the entire reaction is over in an extremely short time.

Explosions can be classified into two categories: *deflagrations* (*flames*) which proceed with relatively small speeds (lower than the speed of sound) and *detonations* (shock waves) which occur faster than the speed of sound.

The flame in a Bunsen burner is a controlled explosion of hydrocarbon-air (oxygen) mixtures and the flame speeds are around 100 cm s^{-1}. In the engine of a car where a compressed mixture of hydrocarbons and air is ignited by a spark, the flame speed is 1000 cm s^{-1}. When the reaction goes out of control we get detonations where flame speeds are of the order of 10^5 cm s^{-1}; this is indeed what happens when there is *knock* in the engine. Knocks destroy the engines, and chemical additives like lead tetraethyl are added to petrol as *anti-knocking agents* to slow down the reaction.

In flames as well as detonations, reactions occur so rapidly as not to allow any heat of reaction to escape from the reaction vessel. The temperatures attained in flames depend on the chemical reactions employed. For example, one of the hottest flames (5000 K) is produced by the reaction,

$$H_2 + F_2 \rightarrow 2 HF \quad \Delta H^\circ = -136 \text{ kcal mol}^{-1}$$
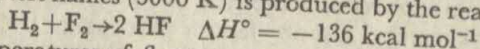
At high temperatures of flames, atoms, radicals and other unusual species are present in large proportions.

Many common reactions become explosive under certain conditions. Thus, the reaction of H_2 and O_2 to give H_2O,

$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$$
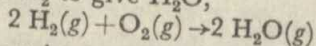
is highly explosive at certain pressures of reactants. Many of the high *explosives* and *detonators* employ substances like metal azides, MN_3, which decompose violently to give nitrogen.

13.11 STUDY OF FAST REACTIONS

13.11.1 Flow and Mass Spectral Methods

Besides explosions and combustion reactions, there occur in solution many reactions that proceed very rapidly—with rate constants as high as 10^{10} s^{-1}. Experimental observations of these reactions have to use detection devices that can monitor very rapid changes in the properties of the reactants/products. Such monitoring methods usually use techniques such as spectroscopy, optical rotation or conductivity. The reactants of interest may be allowed to flow at controlled rates and intersect at a given 'reaction' zone. In a study of the rapid reaction

$$H_2CO_3 \rightarrow H_2O + CO_2$$
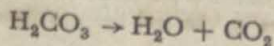
aqueous solutions of sodium bicarbonate and hydrochloric acid are mixed in equivalent amounts, and the electrical conductivity of the solution is measured as a function of time as calculated by the flow rate. The reaction follows a first-order rate with a rate constant of 21 s^{-1}. The resistance increases with time as the conducting acid decays to produce carbon dioxide.

Gas-phase reactions between ions and molecules are extremely fast, often occurring with rate constants as high as 10^{12} s^{-1}. These reactions are conveniently studied using a mass spectrometer. Positive ions of a reactant species are generated and allowed to react with the other reactant molecules, producing secondary ions. The ratio of the mass spectral currents of the primary and secondary ions are experimentally measured. For this measured ion current ratio, a second-order rate constant can be calculated. For the reaction $H^{+}_{2} + H_{2} \rightarrow H^{+}_{3}, + H$, measurement of the ion-current ratio yields a rate constant of 1.7×10^{12} litre mol^{-1} s^{-1}, an extremely rapid reaction indeed.

Other techniques such as polarography, rotating-sector method and magnetic resonance have also been utilised in studying reactions that proceed to completion within microseconds.

13.11.2 Relaxation Methods

When a reaction is disturbed from its equilibrium position suddenly such that the change produced from the equilibrium concentration is, Δx, the system will relax back into equilibrium by a first-order process, characterised by a ' *relaxation time* ',

$$d(\Delta x)/dt = \Delta x/\tau \quad \text{or} \quad \Delta x/\Delta x_0 = \exp(-t/\tau)$$

where Δx_0 is the initial change and Δx is the change at time t. The relaxation time, τ, is a function of the forward- and backward-rate constants. If the time dependence of the relaxation back to equilibrium were studied, the rate constants can be evaluated. Generally, the system in equilibrium is perturbed by means of a sudden and short-lived change in temperature, pressure, or electric field; and the approach to the new equilibrium is measured by spectroscopic, conductivity or other such rapid methods. A ' relaxation ' study of the ionisation equilibrium of acetic acid

$$HA + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_3O^+ + A^-$$
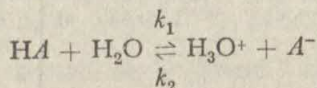
gave a value of $k_1 = 8 \times 10^5$ s^{-1} and $k_2 = 4.5 \times 10^{10}$ litre mol^{-1} s^{-1}.

13.12 MOLECULAR BEAM REACTIONS

In our analysis of the kinetics of reactions, we had so far been taking a macroscopic approach, viz. the entities k, E_a and A all pertain to a large assembly of molecules. The relationship of the rate constant to the molecular world would be of help in developing an insight into what happens at the molecular level during a reaction.

In a collection of molecules, there is a distribution of energy in such a way that a large number have energies corresponding to the average value, with some molecules possessing higher energies and some lower. Molecules are also not stationary, but are constantly colliding with each other. Some of these collisions, where no appreciable energy is transferred, are fruitless from the

reaction point of view. Some others where the energy exchange is large might result in the formation of the products. The rate constant of a reaction, k, is a measure of the probability of a reaction, statistically averaged over a distribution of molecular energies. From this viewpoint, it is desirable to define a microscopic or molecular equivalent of the rate constant, where the initial energy will be an important component. One defines the rate constant as the product of the mean velocity v_r of the reactants, and σ_r a term referred to as the *reaction cross-section*:

$$k = \sigma_r v_r$$

where the units of k, σ_r and v_r are cm^3 molecule^{-1} s^{-1}, cm^2 molecule^{-1}, and cm s^{-1} respectively. The values of σ_r depend on the initial energies of the reactant, and depending on this, a spectrum of values for k is obtained, which when properly averaged gives the macroscopic rate constant k.

The reaction cross-section is, thus, the fundamental entity closer to the molecular world than the rate constant is. One of the ways by which one can directly determine the values of the reaction cross-section as a function of the initial translational (and internal) energy of the reactants involves the use of *molecular beams*.

In the method of molecular beams, the two reactant molecules are separately collimated into beams and allowed to intersect at right angles. The pressure in the reaction vessel is maintained at about 10^{-6} mm, which has the advantage of eliminating any collisions occurring before the beams intersect at the reaction zone. Suitable velocity filters can also be used in the beam paths, so as to restrict the energy of the reactant molecules to a pre-determined range. A schematic diagram of the apparatus is shown in Fig. 13.10 The reaction is allowed to occur at the intersection zone, and the number of product molecules emanating is counted by using suitable detectors that can be made to scan through various angles. From this on the spot analysis of the products, one can directly determine the collision cross-section of the reaction.
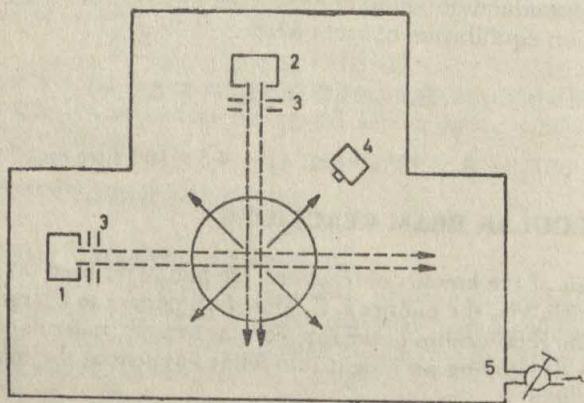
Fig. 13.10 Schematic diagram of a molecular beam apparatus. 1 and 2 are the reactants sources, 3 the slits and velocity selection filters, 4 the detector, 5 the high vacuum pumping system, and the circle is the *reaction zone*.

Several finer details of molecular reaction processes have been unfolded by the molecular beam technique. The most conveniently studied reactions have been between alkali metals and halogens. Here one finds that the chemical energy released in the reaction appears not as translational, but as the (internal) rotational and vibrational energies of the products. It is also seen that the reaction proceeds *via* the formation of an ion-pair, comprising the alkali metal cation and an anion formed through an electron capture by the substrate. This electron transfer model was proposed over thirty years ago and has now received experimental support by molecular beam kinetics.

In recent times, mass spectrometers are being used increasingly as detectors in molecular beam experiments. Mass spectrometers have the capability of being highly efficient analysers of many chemical species, and thus have vastly widened the scope of the molecular beam technique to study diverse reactions.

SUGGESTED READING

F. BASOLO and R. G. PEARSON, *Mechanisms of Inorganic Reactions,* John Wiley, New York, 1958.

A. A. FROST and R. G. PEARSON, *Kinetics and Mechanism,* John Wiley, New York, 1961.

K. B. HARVEY and G. B. PORTER, *Introduction to Physical Inorganic Chemistry,* Addison-Wesley, Reading, Mass., 1963.

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PROBLEMS

13.1 A 22·4 litre vessel contains 0·76 mm of ozone at 25°C. What is the concentration of oxygen atoms needed in this container so that the reaction

$$O + O_3 \rightarrow 2O_2 \quad k = 1·5 \times 10^7 \text{ litre mol}^{-1} \text{ s}^{-1}$$
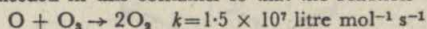
can proceed with a rate 0·15 mol litre^{-1} s^{-1}, expressed in terms of ozone? What will be rate of formation of oxygen under these conditions?

13.2 The rate constant for the reaction $CO_2 + OH^- \rightarrow HCO_3^-$ in aqueous solution is 4×10^3 litre mol^{-1} s^{-1}. Calculate the number of moles of CO_2 and OH^- used up and HCO_3^- formed per second when $[CO_2] = 10^{-6}$ mol litre^{-1}, $[OH^-] = 10^{-1}$ mol litre^{-1}.

13.3 Hydrolysis of tertiary butyl bromide yields tertiary butyl alcohol according to the following reaction: $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$. The following data are obtained at 25°C:

$(CH_3)_3C$—Br mol litre^{-1}	0·1039	0·0859	0·0701	0·0529	0·0270	0·0142
t, hr	0	4·1	8·2	13·5	26·0	37·3

What is the order of the reaction? Also, calculate the specific rate constant and $t_{\frac{1}{2}}$.

13.4 By what factor would the rate of a reaction change when the temperature of a reaction system changes from 27° to 127°C and the activation energy (E_a) of the reaction is: (a) 100 kcal, (b) 10 kcal, and (c) 0 kcal.

13.5 If the rate of a reaction changes by a factor of 2 for a ten degree rise in temperature from 25° to 35°C, what is the activation energy of the reaction?

13.6 In the photodissociation of hydrogen iodide, 500 cal of radiant energy at 48310 cm^{-1} decomposes 0·92 g of HI. What is the quantum yield (number of molecules decomposed per photon) in the decomposition reaction?

13.7 $t_{\frac{1}{2}}$ for decomposition of U^{238} is $4·5 \times 10^9$ years. How many atoms of uranium should we expect to disintegrate per day?

13.8 Gaseous ammonia decomposes on hot tungsten surface to yield nitrogen and hydrogen when the tungsten surface is heated to 1100°C. If the following data on $t_{\frac{1}{2}}$ for the de-

composition were collected, calculate the order of the reaction.

initial pressure of NH_3, mm	300	200	100	50
$t_{\frac{1}{2}}$ min		8·6	5·7 2·9	1·4

13.9 Calculate the activation energy in the following cases:

(a) Decomposition of dibromosuccinic acid in aqueous solution.

Temp.	15°C	60°C	101°C
k	$9 \cdot 67 \times 10^{-6}$	$6 \cdot 54 \times 10^{-4}$	$3 \cdot 18 \times 10^{-2}$

(b) Decomposition of nitrogen pentaoxide vapour.

Temp.	25°C	45°C	65°C
k	$3 \cdot 46 \times 10^{-5}$	$4 \cdot 19 \times 10^{-4}$	$4 \cdot 87 \times 10^{-9}$

13.10 Experimental observations of the reaction system involving decomposition of ozone $2O_3(g) \rightleftharpoons 3O_2(g)$ show that the rate law can be expressed as

$$\frac{-d[O_3]}{dt} = k \frac{[O_3]^2}{[O_2]}$$

What mechanism would you suggest for the reaction that is consistent with the observed rate law?

13.11 What is the difference between a steady-state process and an equilibrium process?

13.12 Salicylic acid is known to be hydrogen bonded as shown. When the acid is shaken with D_2O, the two hydrogen atoms of the side chain groups can be replaced by deu-

terium atoms. It has been found that the rates of exchange of hydrogen and deuterium are different. One exchanges with a rate constant of 10^{-1} s^{-1} and the other has a rate constant of 10^{-5} s^{-1}. Which atom exchanges slowly and which fast?
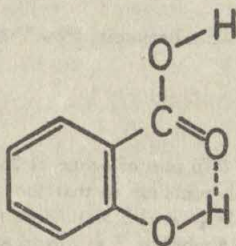
13.13 The small amount of C^{14} present in any material decays radioactively by a first-order rate law, with a half-life of 5,568 years. In an attempt to find out the age of an ancient skull in a cave, C^{14} decay rates were measured. A 5 g sample of carbon obtained from the ancient skull showed 30 per cent as much radioactivity as a 5 g sample of carbon from a very recent specimen of bones. Estimate, using first-order kinetic expressions, the age of the ancient skull.

13.14 Show that the time required for completion of 99.9 per cent of a first-order reaction is ten times that required for one-half of the reaction to occur.

13.15 It is observed that 5 hours are needed to dissolve a 1 cm cube of NaCl in large quantity of water. Calculate the time required for dissolution, if the cube is ground to a powder containing 10^{16} (equal-sized) spheres. Assume that the dissolution time is proportional to the initial area of contact between NaCl and water.
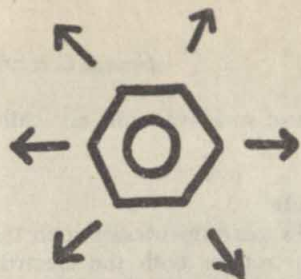
14

Reactions of
Carbon Compounds

Our experiments are not carried out to decide whether we are right, but to gain new knowledge. It is for knowledge's sake that we plow and sow.

R. WILLSTATTER

Chemical reactions are essentially bond-breaking and bond-making processes. These two processes may occur at different times and in discrete steps or they may occur simultaneously in a concerted manner. Breaking a bond requires energy while bond formation is accompanied by release of energy. In organic reactions, covalent bonds are broken to give rise to reactive intermediates which then undergo further transformations. A primary interest of organic chemists is to obtain information on the mechanism of transformation of the reactants to the products. In this chapter, we shall examine different modes of bond cleavage in organic compounds, the nature of some of the reactive intermediates formed as a result of bond cleavage and also some illustrative examples of the different types of organic reactions.

14.1 BREAKING AND MAKING OF BONDS

Covalent bonds in organic compounds are broken in two ways, either homolytically or heterolytically.

14.1.1 Homolytic Cleavage of Covalent Bonds

In a *homolytic cleavage*, the covalent bond breaks symmetrically in such a way that each part retains one electron and the energy needed for bond fission is supplied either in the form of heat or light.

The odd electron left upon bond breaking on each fragment is unpaired. An atom or a group of atoms possessing an odd electron is

$$-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}- \longrightarrow -\underset{|}{\overset{|}{C}}\cdot + \cdot\underset{|}{\overset{|}{C}}-$$

called a *free radical*. The odd electron is generally represented by a dot just as one represents the charge on an ion by a plus or minus sign. Homolytic
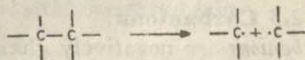
cleavage leads to the formation of free radicals and such reactions are called either homolytic or *radical reactions*.

14.1.2 Heterolytic Cleavage of Covalent Bonds

In the *heterolytic* type of cleavage, the bond breaks unsymmetrically such that one of the parts retains both the electrons which originally constituted the bond between the two fragments. Heterolytic cleavage results in the formation of ions, and reactions in which bonds are broken heterolytically are referred to as *ionic reactions*.
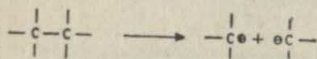
14.2 REACTION INTERMEDIATES

A majority of organic reactions that have been studied so far involve the formation of reactive intermediates and these play an important role in the overall process. Reaction intermediates are short-lived species and are formed either by the decomposition of the organic substrate or by the attack of different reagents on these substrates, and as the name suggests, are species that occur in the chemical reaction as intermediates in the transformation of reactants to products. Such intermediates are hard to isolate in many cases due to their unstable nature. Some of the common reaction intermediates are *radicals*, *carbonium ions* and *carbanions*.

14.2.1 Radicals

As has already been mentioned carbon radicals are formed due to the homolytic cleavage of carbon-carbon single bonds. They are neutral (uncharged) species and are reactive due to their tendency to gain electrons. A few stable free radicals are known, although free radicals, in general, are unstable. The exact type of hybridisation of the carbon atom bearing the odd electron is not clearly understood. A carbon radical may be either pyramidal or planar as shown above.

sp³ (Pyramidal)   sp² (Planar)
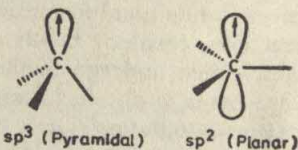
14.2.2 Carbonium Ions

Carbonium ions are *carbon cations* and can be regarded as fragments of organic molecules in which an atom or a group of atoms has been removed together with a pair of bonding electrons in a heterolytic type of cleavage. The hybridisation of the carbon atom bearing the positive charge is generally sp^2 and hence the ion is planar.
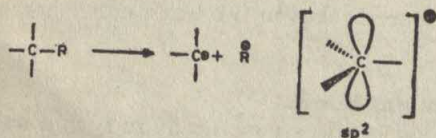
14.2.3 Carbanions

Carbanions are negatively charged species which are formed as a result of a heterolytic bond fission. The other product of the heterolytic fission is the positively charged fragment. In the heterolytic fission, the organic fragment with the carbon atom carrying negative charge is called a carbanion. Carbanions are probably pyramidal in shape and an inversion of two

$$-\overset{|}{\underset{|}{C}}-R \quad\longrightarrow\quad -\overset{|}{\underset{|}{C}}\overset{\ominus}{} + R^{\oplus}$$
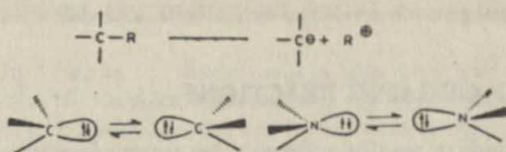
non-planar configurations of carbanions would seem likely as in the case of ammonia inversion.

14.3 CLASSIFICATION OF REAGENTS

Reagents which attack organic compounds may be classified as electrophiles (electron-attracting) and nucleophiles (nucleus-attracting), depending on the electron density at the attacking centre.

14.3.1 Electrophiles
Electrophiles are reagents which attack electron-rich centres in the substrate. Examples of electrophiles include (*i*) positively-charged species, (*ii*) species which are not actually ions themselves but possess an atom or a centre which is electron deficient, and (*iii*) substrates containing polarisable functional groups. Electrophiles in general are Lewis acids (Chapter 11). Some of the common electrophiles are shown below:

$\overset{\oplus}{H}$ (Proton), $\overset{\oplus}{Br}$ (Bromonium ion), BF_3 (Boron trifluoride),

$\overset{\oplus}{R}$ (Carbonium ion), $\overset{\oplus}{N}O_2$ (Nitronium ion), $AlCl_3$ (Aluminium trichloride),

$ZnCl_2$ (Zinc chloride), $FeCl_3$ (Ferric chloride), SO_3 (Sulphur trioxide),

$\overset{\delta\oplus}{R} - \overset{\delta\ominus}{Br}$ (Alkyl bromide), and $R-\overset{\overset{O\,\delta\ominus}{\|}}{\underset{\delta\oplus}{C}}-R$ (Ketone)
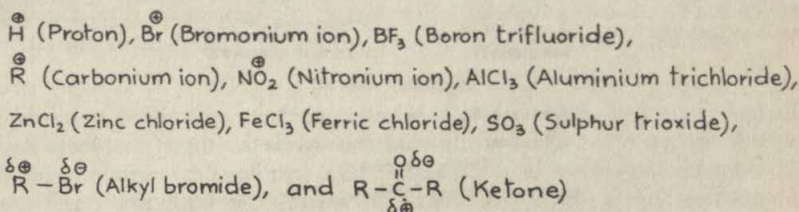
14.3.2 Nucleophiles
Nucleophiles are reagents which are attracted towards electron-deficient centres in the substrate. Negatively-charged species or neutral species containing lone pairs of electrons like water, alcohols, ammonia and amines and all such Lewis bases come under this category. A few common nucleophiles are listed below:

$\overset{\ominus}{H}$ (Hydride ion), $\overset{\ominus}{OH}$ (Hydroxide ion), $\overset{\ominus}{R}$ (Carbanion), $\overset{\ominus}{Cl}$ (Chloride ion),

$\overset{\ominus}{Br}$ (Bromide ion), $\overset{\ominus}{I}$ (Iodide ion), $\overset{\ominus}{CN}$ (Cyanide ion),

$CH_3-COO^{\ominus}$ (Acetate ion), H_2O (Water), NH_3 (Ammonia),

$R-OH$ (Alcohol), $R-NH_2$ (<u>Primary</u> amine), R_2NH (<u>Secondary</u> amine),

R_3N (<u>Tertiary</u> amine), $\overset{\ominus}{RS}$ (Mercaptide ion) and $\overset{\ominus}{HS}$ (Hydrosulphide ion).
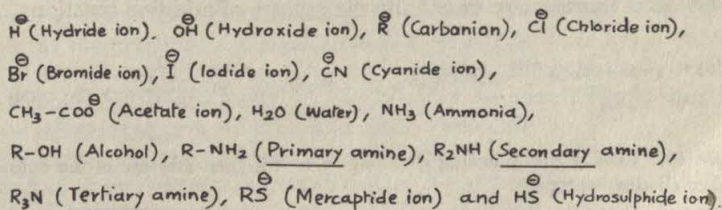
Example 14.1 Which of the following are nucleophiles and which are electrophiles?

(a) $\overset{\oplus}{N}O_2$ (b) $\overset{\ominus}{C}H_3$ (c) SO_3 (d) $\overset{\oplus}{Br}$ (e) H_2O (f) $\overset{\ominus}{OH}$ (g) $\overset{\ominus}{CN}$ (h) $\overset{\ominus}{N}H_2$ (i) $\overset{\oplus}{C}H_3$
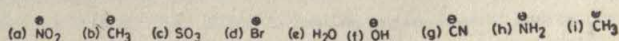
(*a*) Electrophile (*b*) Nucleophile (*c*) Electrophile (*d*) Electrophile (*e*) Nucleophile
(*f*) Nucleophile (*g*) Nucleophile (*h*) Nucleophile (*i*) Electrophile

Thus, it may seem that generally an electrophile is a Lewis acid while a nucleophile is a Lewis base (Chapter 11).

14.4 TYPES OF ORGANIC REACTIONS

Organic compounds generally undergo three types of reactions, (i) *substitution reactions,* (ii) *addition reactions* and (iii) *elimination reactions.* The names are self-descriptive. In substitution reactions, an atom or a group of atoms attached to a carbon atom is replaced by a new atom or a group of atoms. Further classification of substitution reactions is possible based on the nature of the attacking reagent.

$$CH_3-Br + \overset{\ominus}{O}H \longrightarrow CH_3-OH + Br^{\ominus}$$

Methyl bromide   Methanol
(Nucleophilic substitution)

Benzene   Nitrobenzene
(Electrophilic substitution)

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3-Cl + HCl$$

Methane   Methyl chloride
(Radical substitution)

A reaction in which two molecules combine to yield a single product is called an addition reaction and is characteristic of unsaturated compounds. *Addition reactions* can be classified as *nucleophilic, electrophilic* and *radical addition,* depending upon whether the reaction is initiated by a nucleophile, electrophile or radical, respectively. Also, there are numerous examples of *addition reactions* known, which are classified as concerted *cycloadditions* and which do not come under the above types.
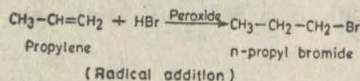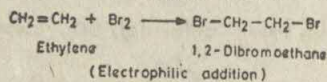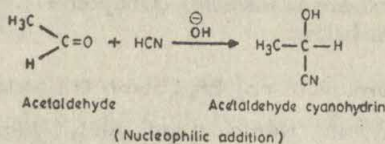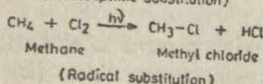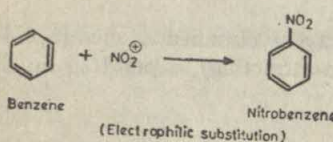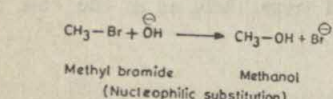
$$\underset{H}{\overset{H_3C}{>}}C=O + HCN \xrightarrow{\overset{\ominus}{OH}} H_3C-\underset{CN}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-H$$

Acetaldehyde   Acetaldehyde cyanohydrin
(Nucleophilic addition)

$$CH_2=CH_2 + Br_2 \longrightarrow Br-CH_2-CH_2-Br$$

Ethylene   1,2-Dibromoethane
(Electrophilic addition)

$$CH_3-CH=CH_2 + HBr \xrightarrow{Peroxide} CH_3-CH_2-CH_2-Br$$

Propylene   n-propyl bromide
(Radical addition)

Elimination reactions are essentially the reverse of addition reactions.

$$CH_3-CH_2-Br + NaOH \xrightarrow{-HBr} H_2C=CH_2$$

Ethyl bromide

$$CH_3-CH_2-OH \xrightarrow[-H_2O]{\overset{\oplus}{H}, \text{ Heat}} CH_2=CH_2$$

Ethanol
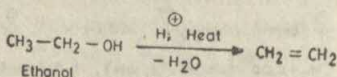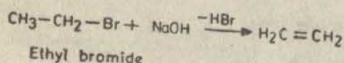
Example 14.2 Classify the following reactions as to whether they are of the substitution, addition or elimination type:

(a) $CH_3-\underset{Br}{\overset{|}{CH}}-CH_2-Br + KOH \longrightarrow CH_3-C\equiv CH$

(b) $CH_3-CH_2-Cl + KOH \longrightarrow CH_3-CH_2-OH$

(c) $CH_3-CH=CH_2 + Br_2 \longrightarrow CH_3-\underset{Br}{\overset{|}{CH}}-CH_2-Br$

(d) $CH_3-\overset{O}{\overset{||}{C}}-H + HCN \xrightarrow{\overset{\ominus}{OH}} CH_3\cdot\underset{CN}{\overset{}{CH}}\cdot OH$

(e) $C_6H_6 + H_2SO_4 \longrightarrow C_6H_5\cdot SO_3H$
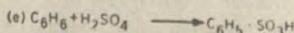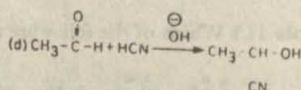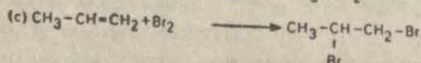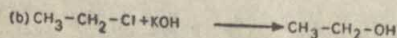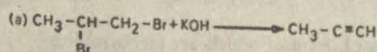
(a) Elimination (b) Substitution (c) Addition (d) Addition (e) Substitution

14.5 REACTIONS OF HYDROCARBONS

As mentioned in Chapter 5, hydrocarbons fall into three categories: (*i*) acylic hydrocarbons, (*ii*) alicyclic hydrocarbons and (*iii*) aromatic hydrocarbons. As acyclic or alicyclic hydrocarbons can be subdivided into alkanes, alkenes and alkynes, we shall survey here some of the important reactions of alkanes, alkenes, alkynes, and aromatic hydrocarbons.

14.5.1 Reactions of Alkanes
In general alkanes are chemically inert to many common reagents such as acids and bases. However, reactions of alkanes can be brought about under more vigorous conditions. Oxidation and substitution are the two important reactions of alkanes.

Oxidation reactions: Alkanes react vigorously on ignition with oxygen to form carbon dioxide and water evolving heat. This reaction forms the basis of their use as fuels in domestic gas and in internal combustion engines, since indane gas, petrol and diesel oil consist of alkanes.

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2H_2O$$
$$\Delta H° = -210 \cdot 8 \text{ kcal mol}^{-1}$$
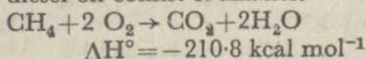
Substitution reactions: Alkanes react readily with chlorine or bromine in the presence of light or on heating to high temperature to form alkyl halides. This reaction is an example of a *free radical substitution reaction*. Thus, photo-chlorination of methane gives methyl chloride and hydrogen chloride.

$$CH_4 + Cl_2 \xrightarrow{\ h\upsilon\ } CH_3Cl + HCl$$
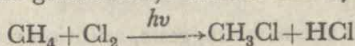
Chlorination of methane does not exclusively give methyl chloride, but also polychlorinated products like dichloromethane (methylene dichloride), trichloromethane (chloroform) and tetrachloromethane (carbon tetrachloride). The yields of these products vary depending on the actual experimental conditions.

$$\begin{array}{ccccc}
CH_4 & \rightarrow & CH_3Cl & \rightarrow & CH_2Cl_2 & \rightarrow & CHCl_3 & \rightarrow & CCl_4 \\
\text{Methane} & & \text{Methyl} & & \text{Methylene} & & \text{Chloroform} & & \text{Carbon} \\
& & \text{chloride} & & \text{dichloride} & & & & \text{tetrachloride}
\end{array}$$
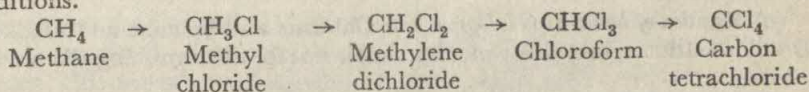
Mechanism for the chlorination of methane: As already pointed out in Chapter 13, a reaction mechanism is a detailed description of a chemical reaction, as the reactants are transformed to products. It is based on experimental observations such as the nature of the products formed, study of reaction rate and stereochemistry. In this case, for instance, we would like to know how a molecule of methane gets converted to methyl chloride.

A reasonable mechanism for the chlorination of methane is one which involves a *free radical chain reaction*. The first step is the photodissociation of chlorine molecules into chlorine atoms (radicals). The chlorine atoms once produced will react with methane to form methyl radical and hydrogen chloride. The methyl radical can then remove a chlorine atom from molecular chlorine forming a molecule of methyl chloride and a new chlorine atom.

$$\begin{array}{ll}
Cl_2 \xrightarrow{\ h\upsilon\ } 2\ Cl\cdot & \text{(INITIATING STEP)} \\
\left. \begin{array}{l} Cl\cdot + CH_4 \rightarrow \cdot CH_3 + HCl \\ \cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot \end{array} \right\} & \text{(PROPAGATING STEPS)}
\end{array}$$
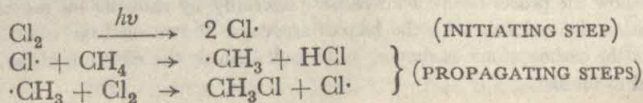
Thus, the chlorine atom which is consumed in one of the steps is being regenerated in a subsequent step and these reactions would be self-propagating without further requirement of chlorine atoms to induce the chlorination of an infinite number of methane molecules. However, in actual practice one finds that these chain propagation reactions are limited by other steps like the combination of methyl radicals with chlorine atoms or of the recombination of chlorine atoms or methyl radicals (chain-termination reactions).

$$\cdot CH_3 + \cdot Cl \rightarrow CH_3\,Cl$$
$$\cdot Cl + \cdot Cl \rightarrow Cl_2 \qquad \Big\} \quad \text{(TERMINATING STEPS)}$$
$$\cdot CH_3 + \cdot CH_3 \rightarrow CH_3\,CH_3$$
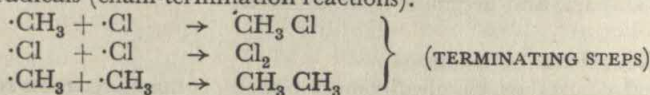
Example 14.3 The reaction of toluene with chlorine is exothermic. Verify this by calculating $\Delta H°$ value of the reaction:

$$C_6H_5\,CH_3 + Cl_2 \xrightarrow{\;hv\;} C_6H_5\,CH_2\,Cl + HCl$$

Bond energies in kcal mol^{-1} are $C - H$ (99), $Cl - Cl$ (58), $C - Cl$ (78), and HCl (103).

$$C_6H_5 - CH_2 - H + Cl - Cl \rightarrow C_6H_5 - CH_2 - Cl + H - Cl$$
$$+\,99 \qquad\qquad +\,58 \qquad -78 \qquad\qquad -103$$
$$+\,136 \qquad\qquad\qquad\quad -171$$
$$\Delta H° = -24 \text{ kcal } mol^{-1}$$
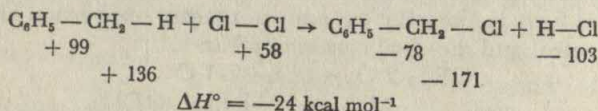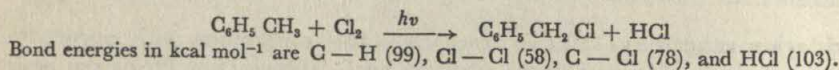
14.5.2 Reactions of Alkenes

The characteristic reactions of alkenes are addition, oxidation and polymerisation reactions.

Addition reactions: As the name suggests, addition reaction involves combination of reactants to give a single product. During this reaction the π bonds present in the starting material get converted into σ bonds. Reagents such as halogens (Cl_2 and Br_2), the hydrogen halides (HCl, HBr, and HI), water and hydrogen add to the carbon-carbon double bond of the alkenes to yield staturated compounds.

(a) *Addition of halogens (Halogenation)* : Chlorine and bromine add to alkenes. Decolourisation of bromine water is a simple test for distinguishing alkenes from alkanes :

$$CH_2{=}CH_2 + Br_2 \longrightarrow Br{-}CH_2{-}CH_2{-}Br$$
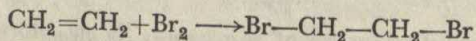
Mechanism: The addition of bromine to an alkene involves a two-step mechanism. The bromine molecule is nonpolar, but under the influence of the electrical field of a nearby carbon-carbon double bond it undergoes *polarisation*, such that the end of the molecule that approaches the double bond becomes partially positive and the other end partially negative. The alkene attracts the more positively charged bromine atom giving the *cyclic bromonium ion intermediate* and a bromide ion. This represents the first step of the reaction. The second step involves the attack by the bromide ion from the rear on the cyclic bromonium ion intermediate.* Of the two steps involved in the overall reaction, the first one will be relatively slow and hence will determine the rate of reaction. It

*We show the processes involved rather pictorially by showing the movement of electron pairs within the molecule with the help of arrows, as shown on page 469. The electrons in Br^- seek the carbon atom as shown, and simultaneously the electrons of the C—Br bond are attracted to the Br^+.

has been observed that in actual practice the reaction follows second-order kinetics, in agreement with this view. Furthermore, stereochemical studies support the view that the addition of bromine to an olefin proceeds in a *trans*-manner.
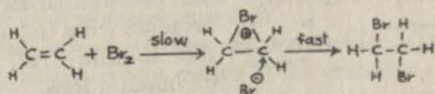
(*b*) *Addition of hydrogen halides* (*Hydrohalogenation*): Hydrogen chloride, hydrogen bromide and hydrogen iodide can add to alkenes to form alkyl halides. For example, ethylene adds to hydrogen bromide to give ethyl bromide.

$$CH_2=CH_2 + HBr \rightarrow CH_3-CH_2-Br$$
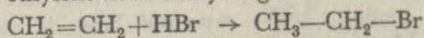
Mechanism: Addition of hydrogen bromide to an unsymmetrical alkene like propene could give rise to two products, namely *n*-propyl bromide and isopropyl bromide, depending upon to which carbon atom of the double bond the hydrogen and bromine get attached. In actual practice, isopropyl bromide is the major product of this reaction. Similarly the reaction of isobutylene with hydrogen bromide gives primarily *t*-butyl bromide even though isobutyl bromide is another possibility.

$$CH_3-CH=CH_2 + HBr \rightarrow$$

$$CH_3 - CH_2 - CH_2-Br + CH_3 - \overset{\overset{\displaystyle Br}{\displaystyle |}}{C}H - CH_3$$
$$\text{\textit{n}-propyl bromide} \qquad \text{Isopropyl bromide}$$
$$\text{(Major product)}$$

$$(CH_3)_2C=CH_2 + HBr \rightarrow$$
$$(CH_3)_2 CH - CH_2 - Br + (CH_3)_3 C - Br$$
$$\text{Isobutyl bromide} \qquad \text{\textit{t}-Butyl bromide}$$
$$\text{(Major product)}$$
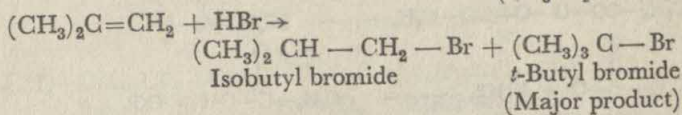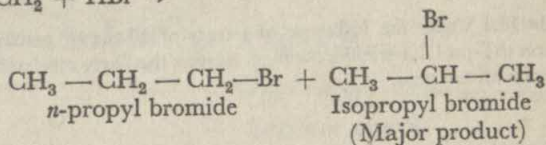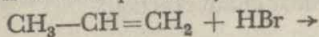
Based on a detailed study, Markownikoff (1871) made an empirical generalisation to predict the direction (orientation) of addition of hydrogen halides to alkenes. This generalisation is known as *Markownikoff's rule* and states as follows. *When a hydrogen halide, HX, adds to an unsymmetrical alkene, the hydrogen of HX goes to that carbon that contains the greater number of hydrogens.* Based on this prediction, the addition of hydrogen bromide to propene and isobutylene should give isopropyl bromide and *t*-butyl bromide respectively. In order to understand the reasons for this, one should examine the mechanism of this type of addition reaction. The addition of hydrogen bromide to an alkene involves two steps: (*i*) the transfer of a proton from hydrogen bromide to the alkene to form a carbonium ion and (*ii*) the combination of the carbonium ion and the bromide ion.
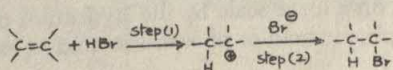
Consider the addition of hydrogen bromide to isobutylene. Two different carbonium ions could be formed by attachment of a proton to one or the other carbon atom of the double bond. The fact that propene is converted to isopropyl bromide and not *n*-propyl bromide would indicate that the *secondary* carbonium

ion is formed at a faster rate than the *primary* carbonium ion and it is more stable. The stability of carbonium ions, in general, follows the order, *tertiary* > *secondary* > *primary*. Likewise, one can explain the preferential formation of *t*-butyl bromide from isobutylene, in terms of the stabilities of the intermediate carbonium ions.

$$CH_3-CH=CH_2+H \longrightarrow
\begin{cases}
CH_3-\overset{\oplus}{O}H-CH_3 \xrightarrow{B\overset{\ominus}{r}} CH_3-CH-CH_3 \\
\text{sec-carbonium ion} \qquad \overset{|}{Br} \\
\qquad\qquad\qquad \text{Isopropyl bromide} \\
\\
CH_3-\overset{\oplus}{C}H-CH_2 \xrightarrow{B\overset{\ominus}{r}} CH_3-CH_2-CH_2-Br \\
\text{primary carbonium ion} \qquad \text{n-propyl bromide}
\end{cases}$$
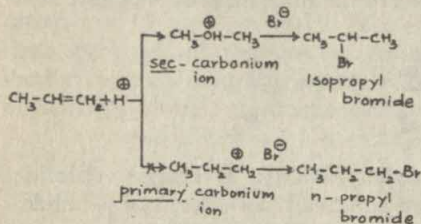
Anti-Markownikoff's Addition: In the case of hydrogen bromide, the mode of addition is reversed in the presence of peroxides. Under these conditions propylene and hydrogen bromide yield *n*-propyl bromide as the major product. This is called anti-Markownikoff's addition. Much of our understanding in this field is due to the pioneering work of Kharasch and his associates around 1933.

$$CH_3-CH=CH_2+HBr \xrightarrow{\text{Peroxide}} CH_3-CH_2-CH_2-Br$$
$$\text{n-Propyl bromide}$$
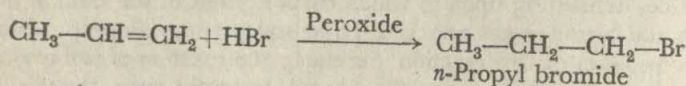
The accepted mechanism for the abnormal addition of hydrogen bromide to alkenes is one which involves a free radical chain reaction.

Example 14.4 Under the influence of a trace of dibenzoyl peroxide 1-pentene reacts with chloroform to form 1,1,1-trichlorohexane. Suggest the likely mechanism for this transformation and indicate all the steps.

$$C_6H_5-CO-O-O-CO-C_6H_5 \longrightarrow 2C_6H_5-\overset{\overset{O}{\|}}{C}-O\cdot$$

$$C_6H_5-\overset{\overset{O}{\|}}{C}-O\cdot + CHCl_3 \longrightarrow C_6H_5-\overset{\overset{O}{\|}}{C}-OH + \cdot CCl_3$$

$$CH_3-CH_2-CH_2-CH=CH_2 + \cdot CCl_3 \longrightarrow CH_3-CH_2-CH_2-\overset{}{CH}-CH_2-CCl_3$$
$$\text{sec-radical}$$

$$CH_3-CH_2-CH_2-\overset{\cdot}{CH}-CH_2-CCl_3 + CHCl_3 \longrightarrow$$
$$CH_3-CH_2-CH_2-CH_2-CH_2-CCl_3 + \cdot CCl_3$$
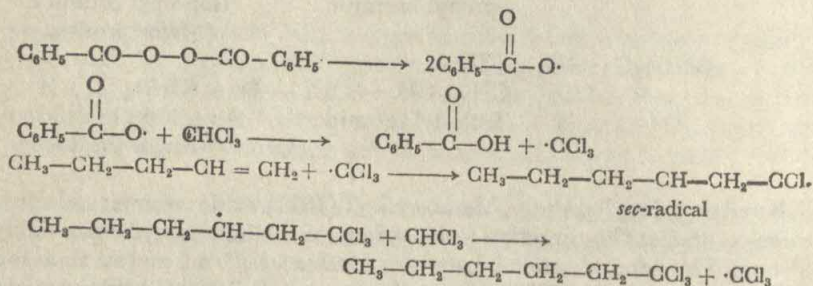
(c) *Addition of water (Hydration)*: The reaction of water with alkenes is extremely slow, but is accelerated in the presence of catalysts like sulphuric acid.

$$\underset{/}{\overset{\backslash}{C}}=\underset{\backslash}{\overset{/}{C}} + H_2O \xrightarrow{H^\oplus} -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{OH}{|}}{\overset{|}{C}}-$$
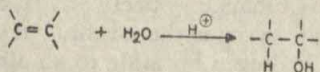
Hydration (addition of water) of alkenes is a commercially important reaction in the preparation of alcohols like ethyl alcohol and *t*-butyl alcohol. These alcohols are prepared on a large scale by the hydration of the corresponding alkenes employing sulphuric acid or phosphoric acid as catalysts.

$$CH_2=CH_2 \xrightarrow[240°]{H_2O,\ 10\%\ H_2SO_4} CH_3-CH_2-OH \qquad \overset{H_3C}{\underset{H_3C}{\diagup}}C=CH_2 \xrightarrow{H_2O,\ 10\%\ H_2SO_4} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$$
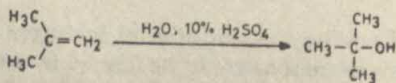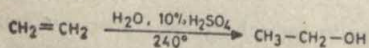
(d) *Addition of hydrogen (Hydrogenation)*: An alkene is converted to an alkane quantitatively when treated with hydrogen in the presence of a catalyst like

nickel, palladium, or platinum. The reaction is used as an analytical tool in determining the number of double bonds in an unsaturated substance.

$$\ce{>C=C< + H2 ->[Cat.] -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{H}{C}}-}$$

The overall reaction is exothermic and the quantity of heat evolved when one mol of an unsaturated compound is hydrogenated is called its heat of hydrogenation. The heat of hydrogenation is a measure of the stability of an alkene. Thus, *trans*-2-butene is more stable than *cis*-2-butene by 1 kcal mol^{-1}.

$$\ce{cis\text{-}2\text{-}Butene ->[H2][Cat.] CH3-CH2-CH2-CH3}$$
n-Butane
$$\Delta H = -28.6 \text{ kcal mol}^{-1}$$

$$\ce{trans\text{-}2\text{-}Butene ->[H2][Cat] CH3-CH2-CH2-CH3}$$
$$\Delta H = -27.6 \text{ kcal mol}^{-1}$$
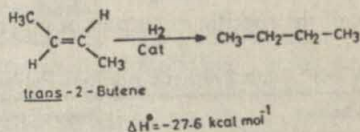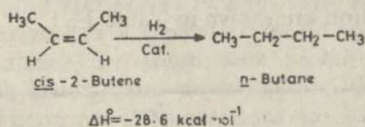
Oxidation reactions: Alkenes can be oxidised by a number of reagents to get a variety of products.

(*a*) *Oxidation by permanganate*: On reaction with dilute or alkaline solution of potassium permanganate, alkenes are converted into 1, 2-diols. Under acidic conditions the products are acids or ketones depending on the structure of the alkene.

$$\ce{CH2=CH2 ->[dil. KMnO4] \underset{\underset{OH}{|}}{CH2}-\underset{\underset{OH}{|}}{CH2}}$$
Ethylene → Ethylene glycol

$$\ce{CH3-CH=CH-CH3 ->[Acidic][KMnO4] 2 CH3-\overset{O}{\overset{||}{C}}-OH}$$
2-Butene → Acetic acid
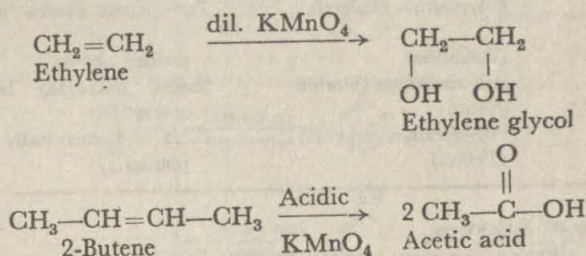
(*b*) *Oxidation by ozone*: The oxidation of alkenes by ozone involves the formation of an addition compound referred to as an ozonide. Ozonides are very reactive and unstable substances. They can be reduced with zinc and acetic acid to aldehydes or ketones or can be oxidised with hydrogen peroxide to acids or ketones. These reactions are illustrated below:
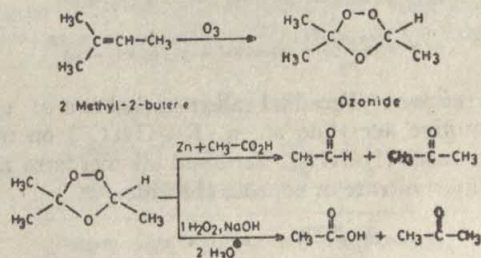
The identification of the products provides a means of finding the position of the double bond in the original alkene.

Polymerisation of alkenes: *Plastics* are important products in organic chemical industry. All of us are familiar with plastic materials like *polyethylene*, *polystyrene* and *polyvinyl chloride*. These products are formed by the linking together of a large number of alkene or substituted alkene molecules in presence of a free radical, or acid, or organometallic catalyst. The alkene molecules are called monomers, and the process is known as *polymerisation*. For example, ethylene polymerises to yield polyethylene.

$$nCH_2=CH_2 \xrightarrow{\text{Catalyst}} (-CH_2-CH_2-)n$$
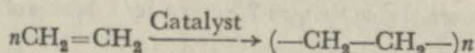
Some of the specific examples of polymerisation are shown in Table 14.1.

Table 14.1 Some Synthetic Addition Polymers

Monomer	Name of polymer	Uses
$C_6H_5-CH=CH_2$	Polystyrene (Styron)	Electrical insulator, foamed plastics, wrapping material
$CH_2=CH-Cl$	Polyvinyl chloride (Koroseal)	Rubber substitute, lacquers
$CH_2=CH-CN$	Polyacrylonitrile	Fabrics
$CH_2=CH-O-CO-CH_3$	Polyvinyl acetate (Vinylite)	Plastic sheets, films and fibres
$CH_2=C-CO_2CH_3$ $\quad\quad\vert$ $\quad\quad CH_3$	Polymethylmethacrylate (Plexiglass)	Transparent sheets, tubes and molded objects
$CH_2=CCl_2$	Polyvinylidene chloride (Saran)	Sheets, packaging bags, seat covers
$CF_2=CF_2$	Polytetrafluoroethylene (Teflon)	Hard and chemically resistant plastics

14.5.3 Reactions of Alkynes

The reactions of alkynes are very similar to that of alkenes except that the terminal alkynes are acidic, and the addition can take place in two stages. Alkynes can be oxidised to carboxylic acids.

Addition reactions: The addition reactions of alkynes are illustrated below:

$$HC\equiv CH \xrightarrow{Br_2} CHBr=CHBr \xrightarrow{Br_2} CHBr_2-CHBr_2$$

$$HC\equiv CH \xrightarrow{HBr} CH_2=CHBr \longrightarrow CH_3-CHBr_2$$

$$HC\equiv CH \xrightarrow[Hg^{+2}]{H_2O, H^{\oplus}} CH_2=CHOH \rightleftarrows CH_3-CHO$$
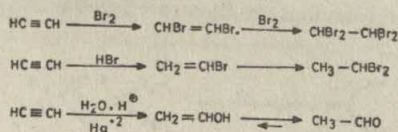
Acidity of terminal alkynes: Terminal alkynes behave as very weak acids $(RC\equiv CH)$. They give acetylide anion $(R-C\equiv C^-)$ on treatment with a strong base like sodamide (NaNH$_2$). Terminal alkynes form metal derivatives with ammoniacal silver nitrate or cuprous chloride.

$$R-C\equiv CH \xrightarrow{NaNH_2} R-C\equiv C Na + NH_3 \quad (R=alkyl)$$

$$R-C\equiv CH \xrightarrow[NH_4OH]{AgNO_3} R-C\equiv C Ag$$

$$RC\equiv CH \xrightarrow[NH_4OH]{CuCl} R-C\equiv C Cu$$
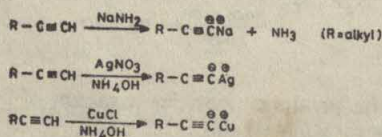
Example 14.5 Write equations for the following reactions; (*a*) the addition HBr to 1-pentene, (*b*) the oxidation product of cyclohexene by ozone followed by H_2O_2 treatment, and (*c*) addition of one mol of HCl to acetylene.

(a) $CH_3-CH_2-CH_2-CH=CH_2$ ⟶ $CH_3-CH_2-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3$

(b) $\xrightarrow[2\ H_2O_2]{1.\ O_3}$ $HO-\overset{O}{\overset{||}{C}}-(CH_2)_4-\overset{O}{\overset{||}{C}}-OH$ (c) $CH\equiv CH \xrightarrow{HCl} CH_2=CH-Cl$
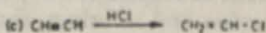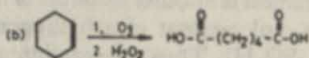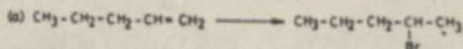
14.5.4 Reactions of Aromatic Hydrocarbons

Benzene is a typical aromatic hydrocarbon. The characteristic reactions of benzene are substitution reactions. Nitration, sulphonation, halogenation, alkylation, and acylation are the common *electrophilic substitution reactions* of benzene. These reactions provide a method of synthesising mono-substituted benzenes. Some examples of these different types of reactions are listed below:
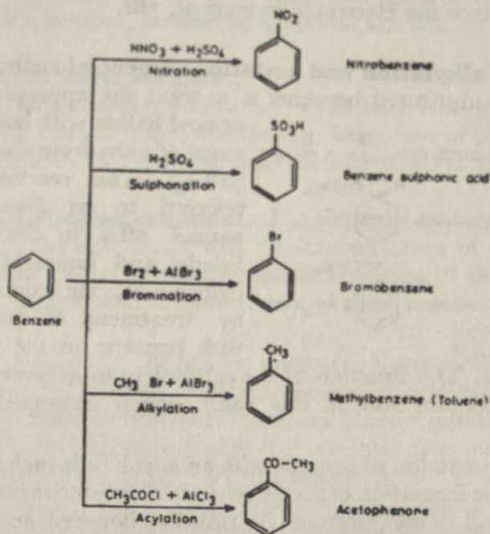
Mechanism of nitration: Nitration of benzene is an *electrophilic substitution* reaction and the electrophilic reagent in this case is the positively charged nitronium ion, $^+NO_2$, produced by treatment of nitric acid with sulphuric acid. The aromatic ring serves as a nucleophile. The reactions leading to the nitronium ion are:

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$
$$HNO_3 + H^+ \rightleftharpoons H_2O + NO_2^+$$
$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$$

$$2H_2SO_4 + HNO_3 \rightleftharpoons H_3O^+ + NO_2^+ + 2HSO_4^-$$
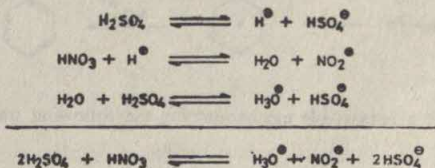
The electrophilic reagent, nitronium ion attaches itself to one of the carbon atoms of the benzene ring to form a carbonium ion which is stabilised by resonance. The loss of the proton from this intermediate gives nitrobenzene.
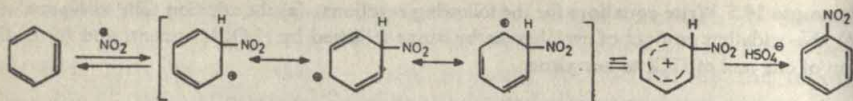
Mechanism of sulphonation: Sulphonation is another example of an electrophilic reaction and it brings about the replacement of a hydrogen atom in benzene with a sulphonic acid group ($-SO_3H$). Thus the reaction of benzene with concentrated sulphuric acid results in the formation of benzene sulphonic acid.

Benzene does not react with bromine in the absence of a catalyst. However, on treatment of benzene with bromine in presence of a catalyst like ferric bromide, bromobenzene is formed. The function of ferric bromide (catalyst) is to bring about the polarisation of Br—Br bond. It may well be that no free ^+Br ion is formed, but that the ferric bromide merely polarises the bromine molecule to produce the electrophilic reagent, ^+Br.

Mechanism of alkylation and acylation: A general method of synthesising alkyl- and acyl-substituted benzenes is to treat the appropriate alkyl halide or acyl halide with benzene in the presence of anhydrous aluminium chloride ($AlCl_3$). This reaction is commonly referred to as *Friedel-Crafts reaction* named after its discoverers, Charles Friedel and James M. Crafts. Isopropylbenzene, for example, is obtained by treatment of isopropyl chloride with benzene in the presence of aluminium chloride. The function of the catalyst is to generate the electrophile (isopropyl carbonium ion in this case) which subsequently reacts with benzene.
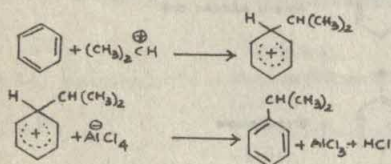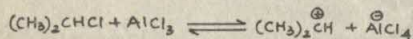
Similarly, the reaction of benzene with an acyl halide such as acetyl chloride would lead to the formation of acetophenone. The reactive intermediate in this case is the acetyl cation, formed by reaction between acetyl chloride and anhydrous aluminium chloride which subsequently reacts with benzene as indicated below:
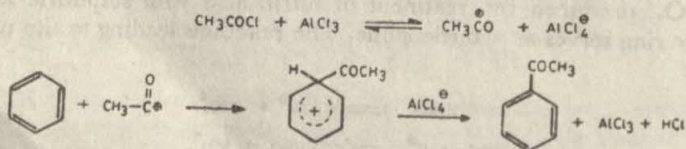
Example 14.6 Suggest a reasonable mechanism for the following transformation:

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{..}{\underset{..}{O}}H + H^{\oplus} \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\oplus}{O}\overset{H}{\underset{H}{<}} \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{}^{\oplus} + H_2O$$

$$\text{[benzene]} + CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{}^{\oplus} \longrightarrow \underset{H}{[\text{ring}]}-C(CH_3)_3 \xrightarrow{H_2O} [\text{ring}]-C(CH_3)_3 + H_3O^{\oplus}$$
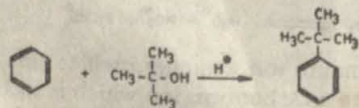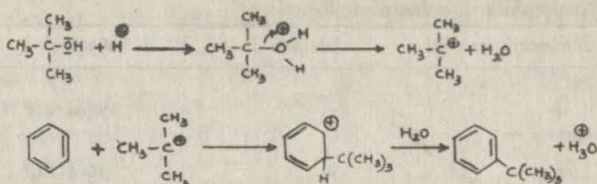
14.6 REACTIONS OF FUNCTIONAL GROUPS

In most organic compounds, carbon atoms may be bonded not only to each other and to hydrogen atoms, but also to other elements such as halogens, oxygen, and nitrogen. In Chapter 5 we have discussed the different types of functional groups and their common and systematic names. Here we shall deal with the important reactions of these functional groups like alkyl halides, alcohols, aldehydes, ketones, carboxylic acids and amines.

14.6.1 Reactions of Alkyl Halides

Alkyl halides (*primary*, *secondary* and *tertiary*) react with a wide variety of substances. Nucleophilic substitution, elimination, formation of Grignard reagent, and reductions are some of the important reactions of alkyl halides.

Nucleophilic substitution reactions: The elements making up the nucleophiles which form the new bond with the carbon atom of the alkyl halide include carbon and the more electronegative elements of the periodic table such as nitrogen, oxygen and sulphur. Some of these reactions are illustrated in Table 14.2.

Mechanisms of nucleophilic substitution reactions: Nucleophilic displacement reactions can proceed through different mechanistic pathways. These are categorised under different headings based on kinetic results as S_N2 (substitution nucleophilic, second order) and S_N1 (substitution nucleophilic, first order). We briefly touched upon these in Chapter 13.

Substitution nucleophilic, second order (S_N2): An example of a nucleophilic substitution of the bimolecular type is the reaction of methyl bromide with sodium hydroxide. It has been observed that the rate of this reaction is dependent on the concentrations of CH_3Br and OH^-, as the rate-determining step involves the interaction of the OH^- with methyl bromide.

$$HO^{\ominus} + CH_3Br \xrightarrow{slow} \left[\overset{\delta\ominus}{HO}\cdots\underset{\underset{H}{|}}{\overset{\overset{H}{\diagup}}{C}}\cdots\overset{\delta\ominus}{Br} \right] \xrightarrow{fast} CH_3OH + Br^{\ominus}$$

Transition state

$$\text{Rate} = R_2 \left[CH_3Br \right] \left[\overset{\ominus}{OH} \right]$$
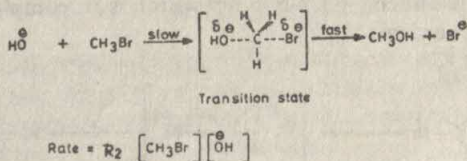
The potential energy diagram representing the relation of the transition state of an S_N2 reaction to the reactants and products is indicated in Fig. 14.1.

When the carbon atom on which the displacement occurs is asymmetrically substituted as in the case of (−) 2-bromobutane, it is possible to investigate the stereochemistry of the reaction. It has been found that the substitution occurs

Table 14.2 Nucleophilic Displacement Reactions

Nucleophilic reagent	Substrate	Product
$\overset{\ominus}{O}H$ Hydroxide ion	CH_3-I	$CH_3OH + \overset{\ominus}{I}$
$\overset{\ominus}{O}CH_3$ Methoxide ion	CH_3-I	$CH_3-O-CH_3 + \overset{\ominus}{I}$
$\overset{\ominus}{S}H$ Mercaptide ion	CH_3-I	$CH_3-SH + \overset{\ominus}{I}$
$CH_3\overset{\ominus}{C}O_2$ Acetate ion	CH_3-I	$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3 +$
$\overset{\ominus}{C}N$ Cyanide ion	CH_3-I	$CH_3-CN + \overset{\ominus}{I}$
$HC\equiv\overset{\ominus}{C}$ Acetylide ion	CH_3-I	$HC\equiv C-CH_3 + \overset{\ominus}{I}$
$\overset{\ominus}{N}H_2$ Amide ion	CH_3-I	$CH_3-NH_2 + \overset{\ominus}{I}$
H_2O Water	CH_3-I	$CH_3-OH + HI$
NH_3 Ammonia	CH_3-I	$CH_3-NH_2 + HI$
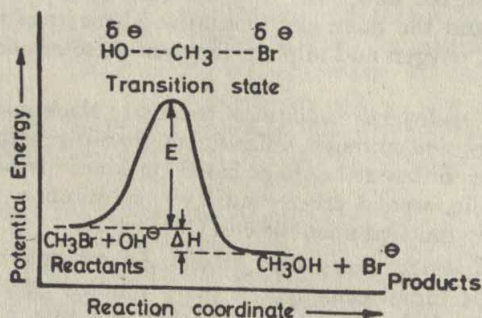
Fig. 14.1 Energy diagram for an $S_N{}^2$ substitution reaction

with inversion to produce $(+)$ 2-butanol which is in complete agreement with the proposed mechanism.
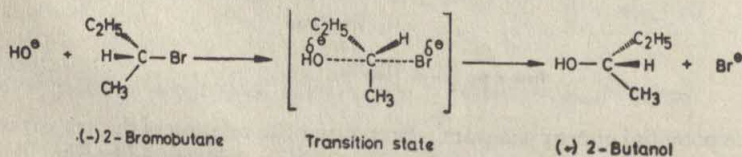
Substitution nucleophilic, first order $(S_N{}^1)$: The reaction between *t*-butyl bromide and sodium hydroxide proceeds by a two-step mechanism as indicated below.

The initial slow step involves the ionisation of *t*-butyl bromide to *t*-butyl-carbonium ion followed by a fast reaction of the carbonium ion with the hydroxide ions present in the medium. The rate of this reaction will be governed by the slowest step namely, the ionisations of the *t*-butyl bromide and hence the reaction would obey first-order kinetics. The energy profile for an S_N1 reaction is shown in Fig. 14.2.

$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br \quad \xrightarrow{slow} \quad CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{}^{\oplus} +Br^{\ominus}$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{}^{\oplus} + \overset{\ominus}{O}H \quad \xrightarrow{fast} \quad CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

$$Rate = k_1 \left[(CH_3)_3 CBr \right]$$
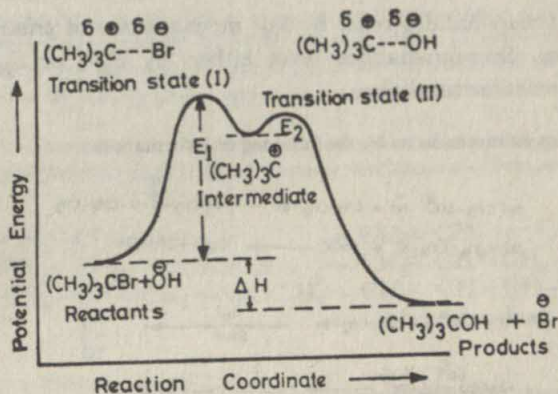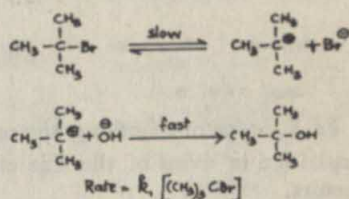
Fig. 14.2 Potential energy change during conversion of *t* - butyl bromide to *t* - butanol

When one carries out a substitution reaction of the S_N1 type reaction employing an optically-active compound such as (−) 2-bromobutane and hydroxide ion, the product is usually a mixture consisting of both (+) and (−) isomers of 2-butanol. Thus, the reaction proceeds with *racemisation* which is expected of a planar carbonium ion intermediate. From this evidence it is clear that a two-step mechanism is involved.
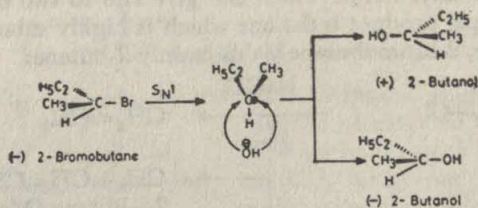
Reactivity considerations: Several cases of the reaction of alkyl halides with nucleophiles have been mentioned in our earlier discussions on substitution reactions. Can we now make some generalisations as to which of these halides will undergo the S_N1 type and the S_N2 type of substitutions?

The rate-determining step in the S_N1 type of reaction is the formation of a carbonium ion intermediate and one can safely conclude that the reactivity of alkyl halides in S_N1 reactions will follow the same order as the stability of the carbonium ions. The decreasing order of reactivity of alkyl halides is indicated in the following:

$$CH_2=CH-CH_2X \gg C_6H_5-CH_2-X \gg CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-X \gg C_2H_5-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-X \gg CH_3-CH_2-X \gg CH_3-X$$

Allyl halide   Benzyl halide   Tert-halide   Sec-halide   Primary-halide   Methyl halide
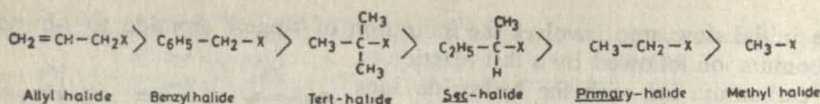
where X = Cl, Br, I

In $S_N{}^2$ type of reactions, the order of reactivity is reversed and this can be explained in terms of the size effects of the substrates and other controlling factors.

$$CH_3—X > primary\text{-Halide} > sec\text{-Halide} > tert\text{-Halide}$$
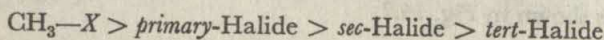
In general, *tertiary*-halides react by $S_N{}^1$ mechanism and *primary*-halides by $S_N{}^2$ mechanism. *Secondary*-halides react either by $S_N{}^1$, or $S_N{}^2$, or both, depending on reaction conditions.

Example 14.7 Suggest mechanisms for the following transformations:

(a) $CH_3-COO^{\ominus} \overset{\oplus}{Na} + CH_3-CH_2-Br \longrightarrow CH_3-\overset{\overset{O}{||}}{C}-O-CH_2-CH_3$

(b) $C_6H_5-CH_2-Cl + NaOH \longrightarrow C_6H_5-CH_2-OH$

(a) $CH_3-COO^{\ominus} + CH_3-CH_2-Br \xrightarrow[\text{Slow}]{S_N{}^2}$

$CH_3COO\overset{\delta\ominus}{-}\underset{\underset{CH_3}{|}}{C}\overset{H}{\underset{}{}}\cdots Br^{\delta\ominus} \longrightarrow CH_3-\overset{\overset{O}{||}}{C}-O-CH_2-CH_3 + Br^{\ominus}$

(b) $C_6H_5-CH_2-Cl \xrightarrow{\text{Slow}} C_6H_5-\overset{\oplus}{CH_2} \xrightarrow[\text{Fast}]{\overset{\ominus}{OH}} C_6H_5-CH_2-OH$
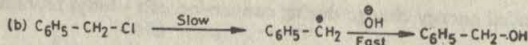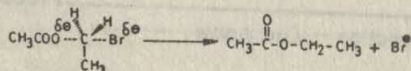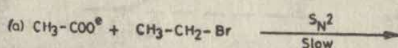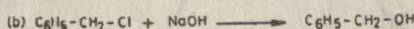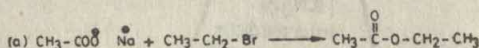
Elimination reactions: Alkyl halides, when heated with a concentrated solution of sodium hydroxide or sodamide are converted into alkenes. The reaction results in the elimination of a molecule of hydrogen halide, and therefore, this reaction is the reversal of the addition of hydrogen halide to alkenes. In the case of an alkyl halide which can give rise to two or more different olefins, the principal product is the one which is highly substituted (*Saytzeff's rule*). For example, 2-bromobutane yields mainly 2-butene:

$$CH_3—CH_2—Cl \xrightarrow[\text{Heat}]{\text{NaOH}} CH_2=CH_2$$

$$CH_3—CH—CH_2—CH_3 \underset{Br}{} \longrightarrow \begin{cases} CH_3—CH=CH—CH_3 \\ \text{2—Butene (Major)} \\ \\ CH_3—CH_2—CH=CH_2 \\ \text{1-Butene (Minor)} \end{cases}$$
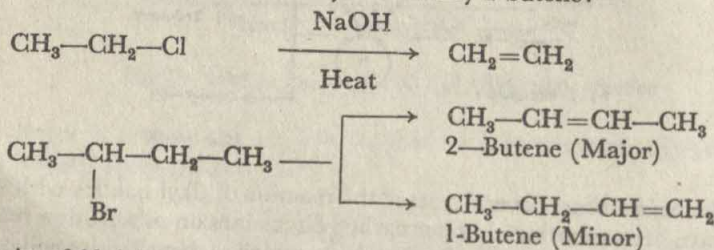
Mechanism of dehydrohalogenation reaction (E_2 *elimination*): It is observed that in dehydrohalogenation reactions, the hydrogen atom that is lost is from a carbon adjacent to the one bearing the halogen atom (β-position) and that the spatial arrangement of the atoms being eliminated (hydrogen and the halogen) is *trans* with respect to each other. In the overall process two bonds are broken, a C—H and a C—Cl bond and a new C—C bond is formed. The bond breaking occurs in such a way that the hydrogen relinquishes both electrons to the carbon atom and the halogen atom leaves with a pair of electrons. The function of the hydroxide ion in this reaction is to help in the removal of the hydrogen atom (C—H bond-breaking process).

Elimination reaction of this type follows second-order kinetics (see Chapter 13) and hence they are referred to as the E_2 *type of elimination.*

$$\text{Rate} = k_2 \left[CH_3-CH_2-Cl \right] \left[\overset{\ominus}{O}H \right]$$
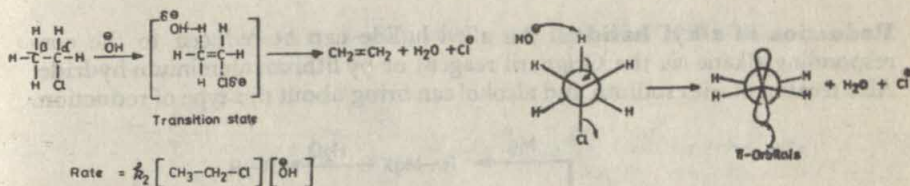
The E_2 elimination reaction proceeds in a *stereospecific* manner and it is generally observed that the eliminating groups or atoms should be *trans* with respect to each other. Such eliminations are also referred to as *trans*-eliminations. It is to be borne in mind that the term *trans* refers to the orientation of the leaving groups and not to be stereochemistry of the resulting olefin.

Example 14.8 Write out three base-catalysed olefin-forming elimination reactions, each of which leads to a different olefin and in which the same combination of base and leaving groups is not employed.

$$CH_3-CH_2-Cl + NaOH \rightarrow CH_2=CH_2$$
$$CH_3-CH_2-CH_2-Br + NaOH \rightarrow CH_3-CH=CH_2$$
$$CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 + NaOC_2H_5 \rightarrow CH_3-CH=CH-CH_3$$
$$\text{(Major product)}$$
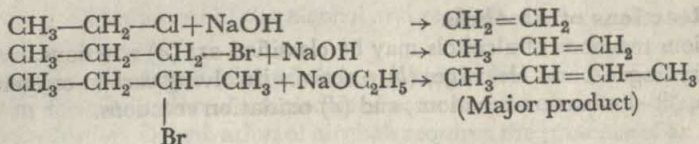
Competition between elimination and substitution reactions: The reaction of ethyl chloride with sodium hydroxide can give rise to two products, ethylene by elimination and ethanol by substitution. Both elimination and substitution are competing reactions, but one can suitably alter the experimental conditions to favour one of these processes. Usually strong bases are required to bring about elimination reactions and the effectiveness of a series of bases
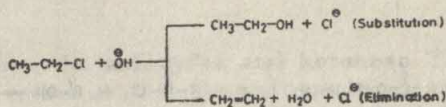
(listed below) is in the order of their base strengths. Eliminations are also favoured at elevated temperatures. On the other hand, weak bases like acetate-ion ($CH_3CO_2^-$), and highly polarisable nucleophiles like iodide (I^-) and mer-

$$\underset{\text{Amide}}{\overset{\ominus}{NH_2}} > \underset{\text{Ethoxide}}{\overset{\ominus}{C_2H_5O}} > \underset{\text{Hydroxide}}{\overset{\ominus}{OH}} > \underset{\text{Acetate}}{\overset{\ominus}{CH_3CO_2}} > \underset{\text{Water}}{H_2O}$$

captide (RS^-) ions tend to give exclusively substitution products.
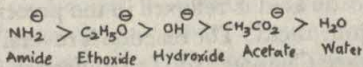
Formation of Grignard reagents: Alkyl halides react with finely divided magnesium metal in dry diethyl ether to form *Grignard reagents* which were named after the French chemist Victor Grignard, the discoverer of this reaction. The structure of a Grignard reagent is written as RMgX for convenience. The carbon magnesium bond in a Grignard reagent is polarised ($R^{\delta-}-Mg^{\delta+}X$) and Grignard reagents behave like strong nucleophiles. They find many applications in synthetic organic chemistry, as enunciated in Chapter 15.

$$R-X + Mg^\circ \xrightarrow{\text{Ether}} R-MgX \qquad (R = alkyl)$$
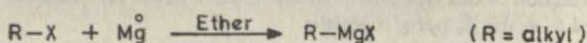
Reduction of alkyl halides: An alkyl halide can be reduced to the corresponding alkane *via* the Grignard reagent or by lithium aluminium hydride. Also treatment with sodium and alcohol can bring about this type of reduction.

$$R-X \begin{cases} \xrightarrow{Mg^\circ} R-MgX \xrightarrow{H_2O} R-H \\ \xrightarrow{Li\,Al\,H_4} R-H \\ \xrightarrow[C_2H_5OH]{Na} R-H \end{cases}$$
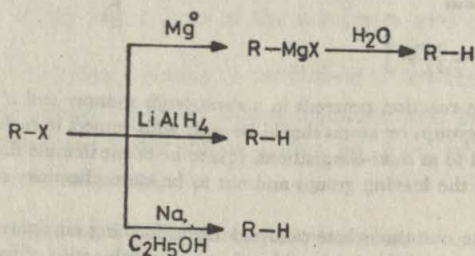
14.6.2 Reactions of Alcohols

The various reactions of alcohols may be classified as: (*a*) reactions involving oxygen-hydrogen bond cleavage, (*b*) reactions involving carbon-oxygen bond cleavage, (*c*) elimination reactions, and (*d*) oxidation reactions.

Oxygen-hydrogen bond cleavage: (*a*) Electropositive metals like sodium and potassium react with alcohols (*primary*, *secondary* and *tertiary*) to give the corresponding alkoxides and hydrogen gas:

$$R-OH + Na^\circ \longrightarrow R\overset{\ominus}{O}\overset{\oplus}{Na} + \tfrac{1}{2}H_2 \uparrow$$

(*b*) Alcohols can be converted into esters by reaction with carboxylic acids or acid chlorides:

$$R-\overset{O}{\overset{\parallel}{C}}-OH + R'-OH \overset{H^\oplus}{\rightleftharpoons} R-\overset{O}{\overset{\parallel}{C}}-O-R' + H_2O \qquad R-\overset{O}{\overset{\parallel}{C}}-Cl + R'-OH \longrightarrow R-\overset{O}{\overset{\parallel}{C}}-O-R' + HCl$$
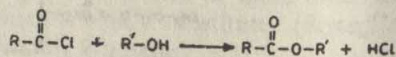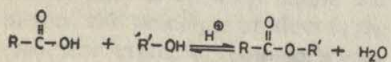
Mechanism of easterification and hydrolysis reactions: In the preparation of methyl acetate, a mixture of methyl alcohol and acetic acid is refluxed in the presence of a small amount of mineral acid like sulphuric acid. The reaction is reversible and attains equilibrium after several hours (see Chapter 10). The hydrogen ion that catalyses the forward reaction (esterification) necessarily catalyses the reverse reaction (hydrolysis) also, and therefore this reversibility is a disadvantage in the preparation of an ester directly from an acid. In many cases, the equilibrium constant for this reaction is unity. If water is removed by slow distillation, the reaction can be used to convert an acid to its ester. On the other hand, in the presence of a large excess of water, hydrolysis of the ester may be made to proceed almost quantitatively.
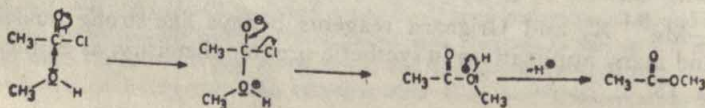
Example 14.9 Write the mechanism of the following reaction indicating the various steps:

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + CH_3-OH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OCH_3 + HCl$$
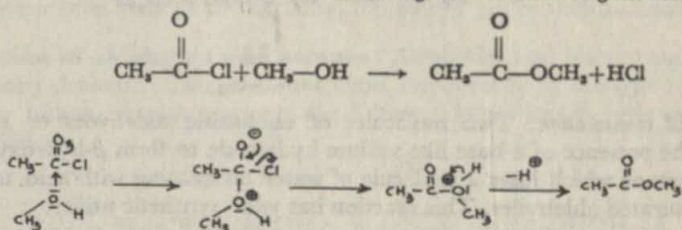
Carbon-oxygen bond cleavage: Many alcohols react with reagents like halogen acids (HX), thionyl chloride ($SOCl_2$) and phosphorus pentachloride (PCl_5) to substitute a hydroxyl group by a halogen. Such reactions are essentially substitution reactions and may proceed through different mechanisms,

$$R-OH \xrightarrow[\text{or } PCl_5]{\text{HCl or } SOCl_2} R-Cl$$
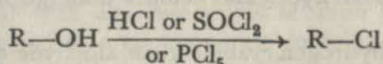
depending on the nature of the alcohol and reagent.

Elimination reactions (dehydration): An alcohol can be converted to an alkene by the elimination of a molecule of water and this process is often referred to as dehydration. Dehydration of alcohols requires the presence of an acid and in many cases the application of heat. Ethanol, for example, is converted to ethylene on treatment with sulphuric acid under suitable conditions.

14.6.3 Reactions of Aldehydes and Ketones

Carbonyl compounds undergo a wide variety of reactions which proceed with comparative ease. The following types of reactions are the most important: (*a*) reactions due to the acidity of α-protons, (*b*) addition reaction, (*c*) reduction, and (*d*) oxidation.

Acidity of α-proton in aldehydes and ketones: The hydrogen atoms attached to the α-carbon in aldehydes and ketones are weakly acidic due to polarisation of the carbonyl function, and this gives rise to some interesting properties.

(*a*) *Keto-enol tautomerism*: Simple aldehydes and ketones *enolise* (keto form going to the enol form) to give structural isomers which exist in equilibrium. The isomers are called tautomers and the phenomenon is known as *tautomerism* (Chapter 5). For example, acetone can exist in equilibrium with its enol form. At room temperature, the enol form is present only in comparatively small amounts.

$$\underset{\text{KETO FORM}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \rightleftharpoons \underset{\text{ENOL FORM}}{CH_2=\overset{\overset{OH}{|}}{C}-CH_3}$$
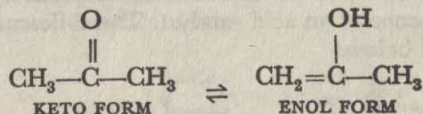
(*b*) *Enolate anions*: The weakly acidic α-hydrogen of an aldehyde or ketone can be removed with bases like sodium hydroxide or sodium ethoxide to give enolate anions which are stabilised by resonance. The following equilibrium exists in the case of acetone.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + C_2H_5\overset{\ominus\oplus}{O}Na \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2\overset{\oplus}{Na} + C_2H_5OH$$

$$\updownarrow$$

$$CH_2=\overset{\overset{\ominus\oplus}{ONa}}{C}-CH_3$$
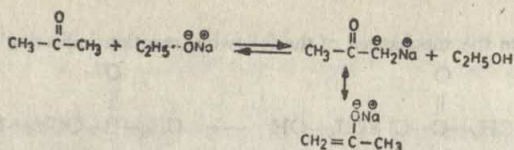
(*c*) *Aldol condensation*: Two molecules of enolisable aldehydes or ketones react in the presence of a base like sodium hydroxide to form β-hydroxy aldehyde or ketone which loses a molecule of water on heating with acid to form α, β-unsaturated aldehydes. This reaction has wide synthetic utility.

$$2\,CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaOH} CH_3-CHOH-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[-H_2O]{H^{\oplus}} CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-H$$

Acetaldehyde
β-Hydroxybutyraldehyde
Crotonaldehyde
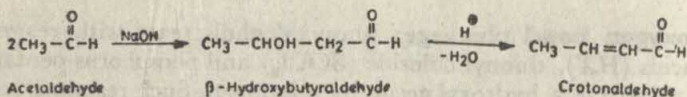
Addition reactions: Aldehydes and ketones undergo nucleophilic addition reactions.

(*a*) The addition of hydrogen cyanide to an aldehyde or ketone takes place readily, in presence of a small amount of sodium hydroxide to give products known as *cyanohydrins*. The role of the hydroxide in this reaction is to generate the cyanide ions and the different steps in the reaction can be formulated as shown below:

R
H
C=O
+ HCN
$\overline{O}H$
R
H
C
OH
CN

Mechanism

HCN + $\overset{\ominus}{O}H$
H_2O + $\overset{\ominus}{C}N$
R
H
C=O
+ $\overset{\ominus}{C}N$
$\bar{\underline{O}}|^{\ominus}$
CN
+ H_2O
OH
+ $\overset{\ominus}{O}H$
Cyanohydrin
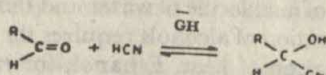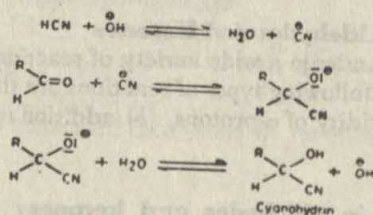
(*b*) Sodium bisulphite adds to aldehydes and some reactive ketones to form the so called, *bisulphite addition compounds*. The reaction is reversible and the addition compounds can be decomposed easily with dilute acid. This addition reaction is used in the separation and purification of aldehydes in particular.

R
H
C=O
+ |S–O Na
OH
SO_3H
OH
SO_3Na
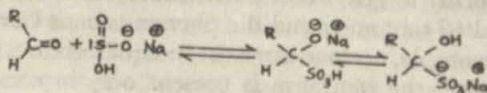
(*c*) Aldehydes and ketones form acetals and ketals respectively, when treated with alcohols in the presence of an acid catalyst. The different steps involved in this reaction are listed below:

$CH_3OH, H^{\oplus}$
$R-\overset{O}{\overset{\|}{C}}-H$
$R-\overset{OH}{C}-O-CH_2-CH_3$
Hemiacetal
$R-\overset{O-CH_3}{C}-O-CH_3$
Acetal

$CH_3OH, H^{\oplus}$
$R-\overset{O}{\overset{\|}{C}}-H$
$R-\overset{OH}{C}-OCH_3$
Hemiketal
$R-\overset{O-CH_3}{C}-O-CH_3$
Ketal

As is evident from this mechanism, all the steps are reversible and one can hydrolyse a ketal back to the carbonyl compound under suitable conditions.

Reduction of aldehydes and ketones : Aldehydes and ketones are reduced to primary alcohols and secondary alcohols, respectively by catalytic hydrogenation or treatment with reagents like lithium aluminium hydride or sodium borohydride.

$$R-\overset{\overset{O}{\|}}{C}-H \rightarrow R-CH_2OH \ ; \ R-\overset{\overset{O}{\|}}{C}-R \rightarrow R-CHOH-R$$

Oxidation of aldehydes and ketones: A characteristic property of aldehydes is their ease of oxidation. Aldehydes give rise to a silver mirror when they are treated with ammoniacal silver nitrate solution (*Tollen's reagent*), whereas ketones do not. Similarly, aldehydes give a red precipitate of cuprous oxide when they are boiled with an ammoniacal solution of a copper tartarate complex (*Fehling's reagent*) or a copper citrate complex (*Benedict's reagent*) but ketones do not undergo these tests. These reactions therefore, find use in distinguishing aldehydes from ketones. Ketones are more difficult to oxidise. When oxidised with powerful oxidising agents such as nitric acid, and potassium

$$R-\overset{\overset{O}{\|}}{C}-H \rightarrow R-\overset{\overset{O}{\|}}{C}-OH$$

permanganate, the bond between the carbonyl carbon and the α-carbon is broken and both the fragments are oxidised to carboxylic acids.

$$R-CH_2-\overset{\overset{O}{\|}}{C}-R' \rightarrow R-COOH + R'COOH$$

Methyl ketones are oxidised by iodine in alkaline solution to give iodoform (CHI_3). Thus, methyl ketones can be identified by this reaction.

$$CH_3-\overset{\overset{O}{\|}}{C}-R + 3I_2 + 4NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O} \ \overset{\oplus}{Na} + CHI_3 + 3NaI + 3H_2O$$

14.6.4 Reactions of Carboxylic Acids

Carboxylic acids undergo several types of reactions such as (*a*) salt formation, (*b*) decarboxylation, (*c*) reduction, and (*d*) formation of acid derivatives.

Salt formation: The dissociation constant (K_a) value of a typical carboxylic acid is about 10^{-4}. They are weaker acids than the common mineral acids, such as hydrochloric acid or sulphuric acid. Carboxylic acids react with sodium bicarbonate solution with the evolution of carbon dioxide to form the corresponding sodium salts. The formation of salts also takes place with inorganic (NaOH) and organic (amines) bases.

$$R-\overset{\overset{O}{\|}}{C}-OH \ \begin{cases} \xrightarrow{NaHCO_3} R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O} \ \overset{\oplus}{Na} + H_2O + CO_2 \\ \xrightarrow{NaOH} R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O} \ \overset{\oplus}{Na} + H_2O \\ \xrightarrow{R_3N} R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O} \ \overset{\oplus}{R_3NH} \end{cases}$$

Decarboxylation: Carboxylic acids when heated strongly with soda lime (NaOH+CaO) lose carbon dioxide to give the corresponding hydrocarbon.

$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[Heat]{CaO + NaOH} R-H \ + \ CO_2$$

Reduction: A carboxylic acid can be reduced to the corresponding *primary* alcohol with lithium aluminium hydride (LiAlH₄).

$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[2\ H_3O^{\oplus}]{1\ LiAlH_4} R-CH_2-OH$$

Formation of acid derivatives: Some of the important derivatives of carboxylic acids include (*a*) acid chloride, (*b*) acid anhydride, (*c*) esters, and (*d*) amides.

(*a*) *Acid chlorides*: Acid chlorides are obtained from carboxylic acids by reaction with phosphorus pentachloride or thionyl chloride.

$$R-\overset{\overset{O}{\|}}{C}-OH$$

$$\xrightarrow{PCl_5} R-\overset{\overset{O}{\|}}{C}-Cl + POCl_3 + HCl$$

$$\xrightarrow{SOCl_2} R-\overset{\overset{O}{\|}}{C}-Cl + SO_2 + HCl$$
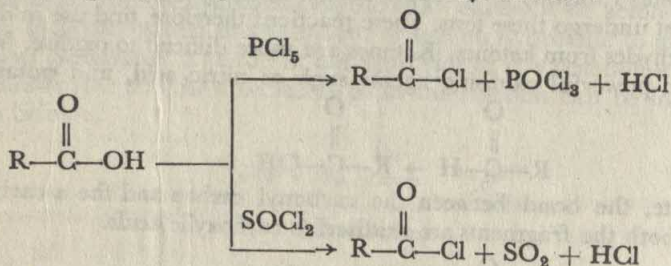
(*b*) *Acid anhydrides*: Acid anhydrides are made from carboxylic acids either directly by dehydration process or indirectly by reacting the sodium salt of the carboxylic acid with the corresponding acid chloride.
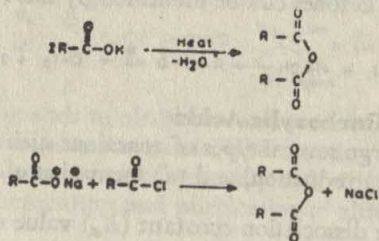
(*c*) *Esters*: Esters can be obtained by the direct reaction of a carboxylic acid and an alcohol in an *equilibrium reaction* (see, reactions of alcohols). However, the equilibrium can be displaced by removal of water continuously. The yield of the ester is not good, in some cases; such esters can be prepared by an indirect method using the reaction of the corresponding acid chlorides and alcohol.
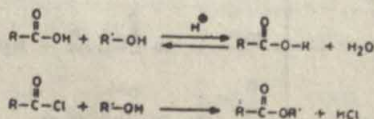
(*d*) *Amides*: Amides are synthesised usually by the reaction between ammonia or amines and acid chloride.

$$R\overset{\overset{\displaystyle O}{\|}}{-C}-Cl+NH_3 \rightarrow R\overset{\overset{\displaystyle O}{\|}}{-C}-NH_2+HCl$$
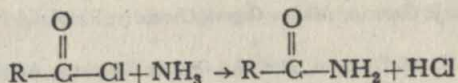
14.6.5 Reactions of Alkylamines

We can consider the reactions of alkyl-substituted amines (*primary*, *secondary* and *tertiary*) under the following headings: (*a*) salt formation, (*b*) reaction with alkyl halides, (*c*) reaction with carboxylic acid derivatives, and (*d*) reaction with nitrous acid.

Salt formation: Aliphatic amines behave like bases and form salts with acids.

$$R-NH_2 + HCl \longrightarrow R-\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$$
$$R_2NH + HCl \longrightarrow R_2\overset{\oplus}{N}H_2\overset{\ominus}{Cl}$$
$$R_3N + HCl \longrightarrow R_3\overset{\oplus}{N}H\overset{\ominus}{Cl}$$
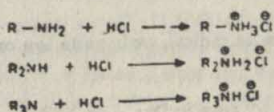
Reactions with alkyl halides: *Primary*, *secondary* and *tertiary* amines can react with alkyl halides to give the corresponding substituted amines as indicated below:

$$R-X + R-NH_2 \longrightarrow R_2NH + HX$$
$$R-X + R_2NH \longrightarrow R_3N + HX$$
$$R-X + R_3N \longrightarrow R_4\overset{\oplus}{N}\overset{\ominus}{X}$$
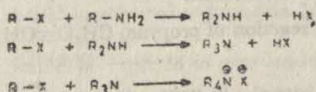
Reactions with acid derivatives: *Primary* and *secondary* amines react with acid chlorides, anhydrides and esters to give amides.

$$R-CO-Cl+R^1NH_2 \rightarrow R\overset{\overset{\displaystyle O}{\|}}{-C}-NHR^1+HCl$$
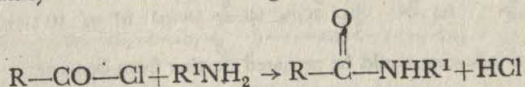
Reactions with nitrous acid: Primary aliphatic amines react with aqueous nitrous acid to yield alcohols with the evolution of nitrogen. *Secondary* amines react quite differently with aqueous nitrous acid, and nitrosoamines are formed in these cases. *Tertiary*-amines, on the other hand give rise to a complex mixture of products.

$$R-NH_2+HONO \longrightarrow R-OH+H_2O+N_2$$
$$R_2-NH+HONO \longrightarrow R_2N-N=O+H_2O$$
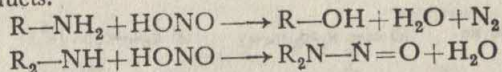
Example 14.10 Suggest a one-step reaction for the synthesis of the following compounds:

(a) $CH_3-CH_2-CH_2-CH_3$, (b) $CH_3-C\equiv C-CH_3$, (c) $CH_3-CH_2-O-CH_3$, (d) $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$, (e) $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_3$

(a) $CH_3-CH_2-CH_2-CH_2-Br \xrightarrow{LiAlH_4} CH_3-CH_2-CH_2-CH_3$

(b) $CH_3-C\equiv \overset{\oplus\ominus}{C}Na + CH_3-I \longrightarrow CH_3-C\equiv C-CH_3$

(c) $CH_3-\overset{\oplus\ominus}{O}Na + CH_3-CH_2-Br \longrightarrow CH_3-O-CH_2-CH_3$

(d) $CH_3-\underset{OH}{CH}-CH_3 \xrightarrow{CrO_3} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ (e) $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + CH_3-NH_2 \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_3$
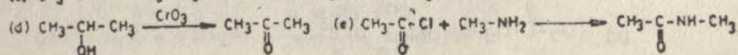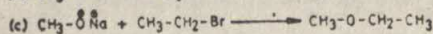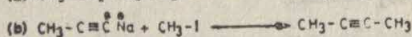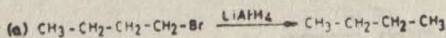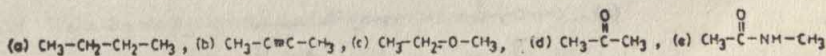
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PROBLEMS

14.1 Name the following species as radical, carbonium ion or carbanion:

(a) $C_6H_5-\overset{\bullet}{C}H_2$ (b) $CH_3-\overset{\ominus}{C}H_2$ (c) $CH_2=CH-\overset{\ominus}{C}H_2$ (d) $(C_6H_5)_3\overset{\oplus}{C}$ (e) $CH_3-\overset{}{C}H-CH_3$ (f) $CH_2=\overset{\ominus}{C}H$

Which of the above are electrophiles and which are nucleophiles?

14.2 Give an example of each type of the following reactions: (a) electrophilic addition, (b) radical addition, (c) base-catalysed elimination reaction, (d) nucleophilic substitution, and (e) electrophilic substitution.
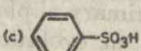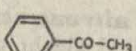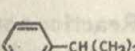
14.3 Write equations for the reaction of propyne, $CH_3C\equiv CH$, with each of the following:

(a) H_2 (excess) and Pd, (b) Br_2 (excess), (c) $NaNH_2$, (d) $Ag(NH_3)_2^{\oplus}$, (e) $Cu(NH_3)_2^{\oplus}$, (f) $H_2O/\overset{\oplus}{H}/Hg^{+2}$

14.4 Write equations for the reactions of CH_3-CH_2-Br with:

(a) $\overset{\ominus}{S}H$ (b) $\overset{\ominus}{C}N$ (c) $\overset{\ominus}{O}C_2H_5$ (d) $\overset{\ominus}{O}H$ (dilute)   (e) Mg^{+} (f) $LiAlH_4$

14.5 Show how the following could be prepared starting from benzene:

(a) [benzene ring]—Br   (b) [benzene ring]—NO_2 (c) [benzene ring]—SO_3H (d) [benzene ring]—$CO-CH_3$ (e) [benzene ring]—$CH(CH_3)_2$

14.6 Write equations for the reactions of cyclohexanol with:

(a) $SOCl_2$ (b) Na   (c) conc. H_3PO_4 (heat)   (d) C_6H_5-COOH ($\overset{\oplus}{H}$)   (e) CrO_3

14.7 Write equations for:

(a) $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H \ + \ KMnO_4 \longrightarrow$

(b) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \ + \ NH_2OH \ \xrightarrow{\overset{\oplus}{H}}$

(c) $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H \ + \ NaHSO_3 \longrightarrow$

(d) $CH_3-\overset{\overset{O}{\|}}{C}-H \ + \ HCN \ \xrightarrow{\overset{\ominus}{O}H}$

(e) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \ + \ CH_3MgI \ \xrightarrow{H_3\overset{\oplus}{O}}$

14.8 Starting with propionic acid, show how the following could be prepared:

(a) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Cl$ (b) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH_2$ (c) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3$

(d) $CH_3-CH_2-CH_2OH$ (e) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}$ $\begin{matrix} \\ O \\ \end{matrix}$

           $CH_3-CH_2-\overset{\|}{\underset{O}{C}}$
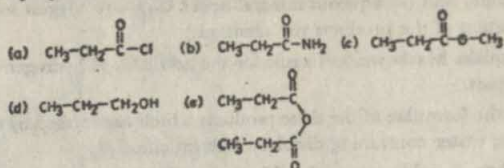
14.9 Compare the behaviour of the th.... amines—aniline, N-methylaniline and N, N dimethylaniline—towards each of the following reagents: (a) dilute HCl, (b) NaNO₂ and aqueous HCl, (c) methyl iodide.

14.10 The reaction of methane with chlorine is exothermic. Verify this by calculating ΔH value of the reaction:

$$CH_4 + Cl_2 \rightarrow CH_3-Cl + HCl$$
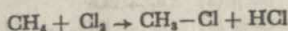
Bond energies (in kcal per mole) are: C—H(101), Cl—Cl(58), C—Cl(80), H—Cl(103).

14.11 Draw energy diagrams for reactions that possess the following features. Label the activation energy and transition state for each stage and the intermediate in the reaction: (a) A one-stage reaction and (b) a two-stage reaction in which the second stage is slower than the first.

14.12 State concisely the kinetic and stereochemical differences between S_N1 and S_N2 reactions.

14.13 Give examples of the following reactions:
(a) Two examples of reactions that should largely give rise to racemisation.
(b) Two examples that should largely lead to inversion (*d*- to *l*- or vice versa) in configuration.
(c) Two examples that would be expected to give rise to retention in configuration (*d*- to *d*- or *l*- to *l*-).

14.14 In the following reaction, label the nucleophile, the substrate and the leaving group. Indicate the mechanism of the reaction.

$CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}$ + $CH_3-CH_2-O-SO_2-$⟨ ⟩ ⟶ $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$ + ⟨ ⟩$-\overset{\ominus}{S}O_3$
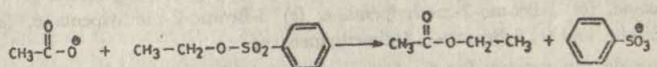
14.15 Write the mechanism for each of the following reactions:

(a) ⟨CH₃⟩ $\xrightarrow[H_2SO_4]{HNO_3}$ ⟨CH₃ ... NO₂⟩ (Major product)

(b) ⟨ ⟩ $\xrightarrow[AlCl_3]{CH_3CH_2COCl}$ ⟨CO—CH₂—CH₃⟩

(c) ⟨NO₂⟩ $\xrightarrow[H_2SO_4]{HNO_3}$ ⟨NO₂ ... NO₂⟩

14.16 Write the mechanism for the following reactions:

(a) $\underset{CH_3}{\overset{CH_3}{>}}C=O$ + HCN $\xrightarrow{\overset{O}{OH}}$ $\underset{CH_3}{\overset{CH_3}{>}}\underset{CN}{\overset{OH}{C}}$

(a) $\underset{CH_3}{\overset{CH_3}{>}}C=O$ + CH_3Li $\xrightarrow{H_3O^{\ominus}}$ $\underset{CH_3}{\overset{CH_3}{>}}\underset{OH}{\overset{CH_3}{C}}$

(c) $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$ $\xrightarrow{H_3O^{\ominus}}$ $CH_3-\overset{O}{\overset{\|}{C}}-OH$ + CH_3-CH_2-OH

(d) $CH_3-\overset{O}{\overset{\|}{C}}-H$ + $2CH_3OH$ $\xrightarrow{H^{\oplus}}$ $\underset{H}{\overset{CH_3}{>}}\underset{OCH_3}{\overset{OCH_3}{C}}$ + H_2O
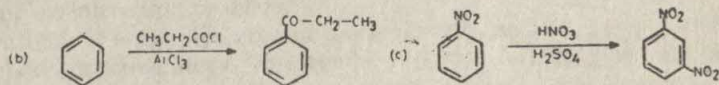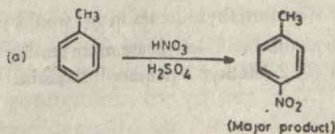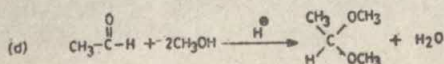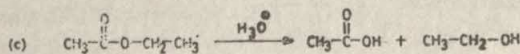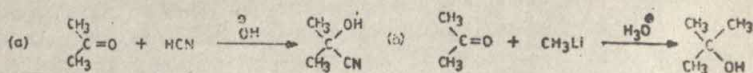
14.17 What are the products you expect when propylene is treated with (a) bromine, (b) hydrogen bromide, and (c) aqueous mineral acid? Can you suggest suitable explanations for the formation of the products you mention?

14.18 State and explain Markownikoff's rule for the addition of hydrogen chloride to unsymmetrical alkenes.

14.19 Write down the formulae of the three products which are formed by reaction of ethylene with bromine water containing dissolved sodium chloride.

14.20 A hydrocarbon A, adds one mole of hydrogen in the presence of a platinum catalyst to form n-hexane. When hydrogen bromide is added, a single bromo compound is formed. Give the structure of A. Show your reasoning, including equations for all reactions.

14.21 A conceivable mechanism for the chlorination of methane involves the following steps:

$$\text{Step (1)} \quad Cl_2 \rightarrow 2Cl\cdot$$
$$\text{Step (2)} \quad Cl\cdot + CH_4 \rightarrow CH_3-Cl + H\cdot$$
$$\text{Step (3)} \quad H\cdot + Cl_2 \rightarrow H\text{-}Cl + Cl\cdot$$

(a) Calculate the ΔH value for each of these steps. (b) Why does this mechanism seem less likely than the accepted one?
Bond energies (in kcal per mole) are: C—H(99), Cl—Cl(58), C—Cl(78) and H—Cl (103).

14.22 When benzene is treated with chlorine in the presence of ultraviolet light, a solid material is obtained. Quantitative analysis of this indicates an empirical formula of CHCl. Molecular mass determination (freezing point depression) gave a value of 300. (a) What is the molecular formula of the product? (b) What is the possible structural formula of the product? (c) What kind of reaction has taken place? (d) Is the product aromatic?

14.23 Photochlorination of methane gives a number of products like methyl chloride, methylene dichloride, chloroform and carbon tetrachloride. Suggest possible mechanisms for the formation of these products.

14.24 Give structures of the product(s) expected from dehydrohalogenation of: (a) 1-Bromohexane, (b) 1-Bromo-2-methylpentane, (c) 3-Bromo-2-methylpentane, (d) 3-Bromopentane, and (e) 3-Bromo-2, 3-dimethylpentane.

14.25 How do you account for the formation of the following compounds? (a) 2-Butene in dehydration of n-butyl alcohol and (b) 2, 3-Dimethyl-2-butene and 2, 3-Dimethyl-1-butene from 3, 3-Dimethyl-2-butanol.
Which of the two dimethylbutenes in (b) would you expect to predominate?

14.26 Predict which alcohol will dehydrate more readily when heated with acid: (a) 2-Methyl-2-pentanol or (b) 2-Methyl-3-pentanol. Explain.
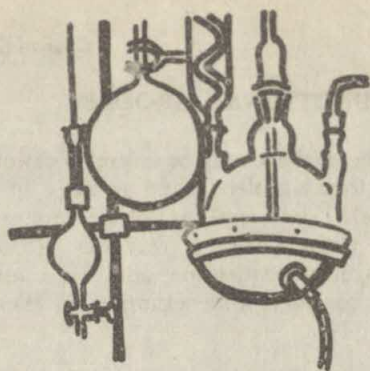
15

Synthesis of
Carbon Compounds

There is excitement, adventure, and challenge, and there can be great art, in organic synthesis.

R. B. WOODWARD

In Chapter 14, we were concerned with some of the basic principles that govern organic chemical reactions. It is the purpose of this chapter to draw together some of the reactions we have discussed earlier and to see how best we can utilise them in the synthesis of organic compounds.

Practising organic chemists synthesise compounds for a variety of reasons. One might desire to confirm the structure of a naturally occurring substance by synthesising it in the laboratory employing known reactions. Another aim might be to prepare compounds which would be expected to have some unusual properties. Quite often it becomes necessary to evolve synthetic procedures for commercially important compounds by routes which are economically feasible. Synthesis may even be attempted for the sheer satisfaction derived in solving an interesting problem.

Synthesis of a complex organic molecule may require several bond-making and bond-breaking steps. The synthesis of *haemin* (red colouring matter of blood), *chlorophyll* (green colouring matter of plants) and *vitamin B_{12}* are few examples of outstanding efforts in this area. In order to gain an understanding of the approaches to the synthesis of organic compounds one has to be familiar with the reactions of different functional groups and the innumerable possibilities of organic transformations. Synthesis of biologically active compounds will also require specific stereochemical control. Thus, a proper choice of reagents and reaction conditions will have to be employed for the synthesis of a *cis*-isomer in preference to the *trans*-isomer, or a *l*-isomer in preference to the *d*-isomer.

489

33

15.1 INTERCONVERSION OF FUNCTIONAL GROUPS

During the course of an organic synthesis, there may be several occasions when we wish to remove a particular group from a molecule and replace it by another (interconversion of functional groups). Functional groups are interconverted employing chemical reactions. The main classes of reactions, which effect functional group interconversions, involve substitution, addition, elimination, oxidation, reduction, etc. We shall consider some examples of these interconversions.

15.1.1 Interconversions of the Carboxyl Group

A carboxyl group ($-CO_2H$) present in organic acids can be transformed to a variety of other functional groups by treatment with suitable reagents. For example, a carboxylic acid on treatment with a base (OH^-) is converted to its anion (RCO^-_2), which is a reversible reaction. Treatment with thionyl chloride or potassium pentachloride converts the acid to the acid chloride. The acid chloride in turn is converted back to the acid on treatment with water, or to the ester on treatment with an alcohol ($R'OH$). The ester can also be directly obtained from the free acid by treating it with alcohol in the presence of a small amount of mineral acid under suitable conditions. Treatment of the acid chloride with the free acid results in the formation of an acid anhydride. The anhydride can also be obtained by the treatment of the acid with a dehydrating agent like phosphorus pentoxide. Hydrolysis of the anhydride will result in the formation of the starting acid. Treatment of either the free acid or its ester with ammonia gives rise to the amide. The amide, on treatment with phosphorus pentoxide, will result in the formation of a nitrile (RCN). Both the amide and nitrile can be hydrolysed back to the starting acid under appropriate conditions. Some of these transformations of the carboxyl group are indicated in Scheme 15.1.

Reduction of a carboxylic acid of its ester employing lithium aluminium hydride gives a primary alcohol. This alcohol can be reverted back to the
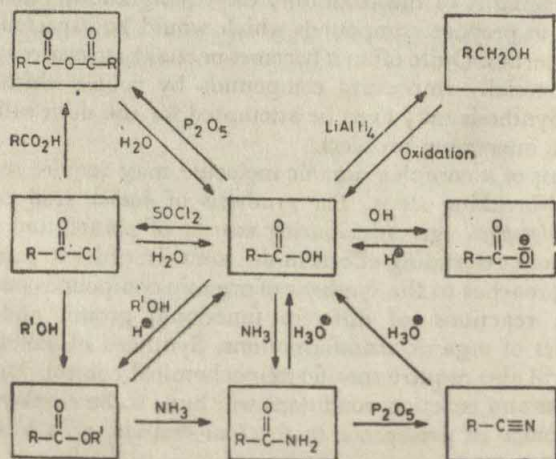
Scheme 15.1 Interconversions of carboxyl derivatives

starting acid by treatment with an oxidising agent like potassium permanganate. Treatment of an alcohol with phosphorus tribromide gives an alkyl bromide and the alkyl bromide itself can give rise to several other products. We have already seen several examples of nucleophilic displacement reactions of alkyl-halides in Chapter 14. One of the reactions that an alkyl halide undergoes is its conversion to a *Grignard reagent*, when treated with magnesium in ether. The Grignard reagent is a powerful synthetic tool and is capable of bringing about a number of functional group transformations as shown in Scheme 15.2. For example, the reaction of a Grignard reagent, RCH_2MgBr, with water results in the replacement of the MgBr group by hydrogen to give a hydrocarbon ($R—CH_3$). The reaction with carbon dioxide, on the other hand,
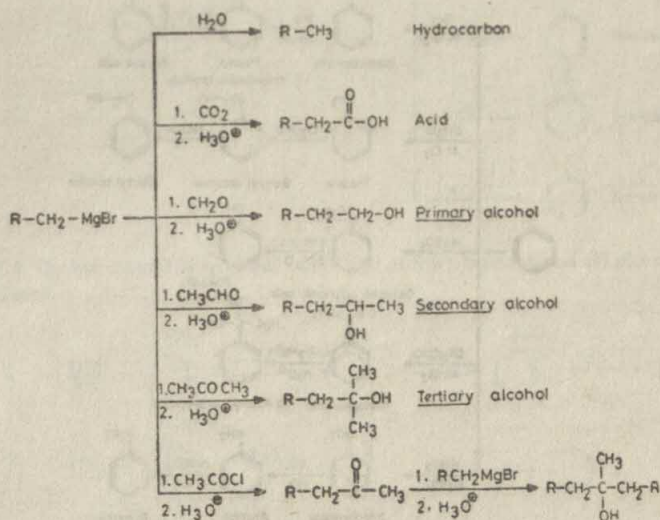
Scheme 15.2 Reactions of Grignard reagents

gives the carboxylate salt of an acid, from which the free acid can be generated by treatment with water and some mineral acid. The reactions of Grignard reagents with carbonyl group compounds such as aldehydes and ketones give rise to primary and secondary alcohols, respectively. The reaction with either an acid chloride or an ester, gives as the end product, a *tertiary* alcohol.

Example 15.1 Prepare 2-methyl-2-butanol from *n*-propanol.
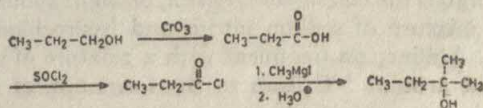
15.1.2 Interconversions of Aromatic Compounds
Several interesting and useful functional group transformations can be brought about in aromatic compounds. Benzene, for example, can be converted to

several of its derivatives employing suitable reactions. Some of these trans-
formations are listed in Scheme 15.3. The reaction of benzene with bromine in
the presence of $FeBr_3$ gives rise to bromobenzene, which in turn can be trans-
formed to benzoic acid through a Grignard reaction. Similarly, benzene can be
converted to toluene through the *Friedel-Crafts* alkylation procedure. Toluene
can be transformed to benzyl chloride through a photo-chlorination procedure
and benzyl chloride in turn can be converted to benzyl alcohol by hydrolysis in
the presence of a base (NaOH). Treatment of benzene with fuming sulphuric
acid, for example, leads to benzenesulphonic acid, which can be ultimately
converted to phenol. On the one hand, benzene on acylation using acetyl
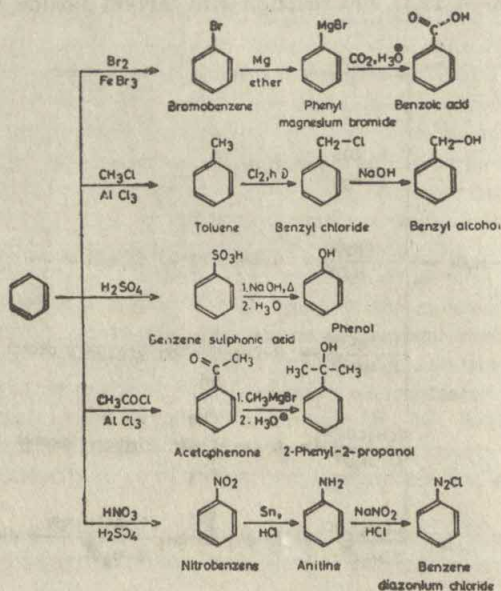
Scheme 15.3 Reactions of benzene and some of its
derivatives

chloride and $AlCl_3$ (*Friedel-Crafts* reaction), gives rise to acetophenone,
which can then be converted to 2-phenyl-2-propanol through a Grignard
reaction. Nitration of benzene, on the other hand will lead to nitrobenzene
which can be subsequently reduced to aniline.

Aniline can be used as the starting material for bringing about a variety of
transformations. One of the reactions which aniline and other aromatic primary
amines will undergo is the *diazotisation reaction*, brought about by treatment with
nitrous acid (a mixture of sodium nitrite and hydrochloric acid is used in
actual practice). Aniline, on treatment with a mixture of sodium nitrite and
hydrochloric acid around 5°C leads to the formation of benzenediazonium
chloride which is not very stable at room temperature. Benzenediazonium
chloride undergoes very facile displacement reaction leading to the formation
of several substituted benzene derivatives. Some of these transformations are
shown in Scheme 15.4. The reaction with water in presence of an acid such as
phosphrous acid, H_3PO_2, for example will give rise to benzene. Similarly,

groups like CN, OH, and halogens can replace the diazonium group ($-N \equiv N^+$), giving rise to the corresponding benzene derivatives.

Scheme 15.4 Reactions of benzenediazonium chloride
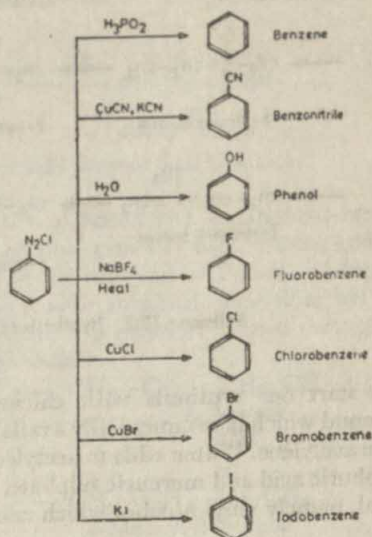
Example 15.2 Outline a possible synthesis of (*a*) phenol from benzene and (*b*) phenylacetic acid from toluene.
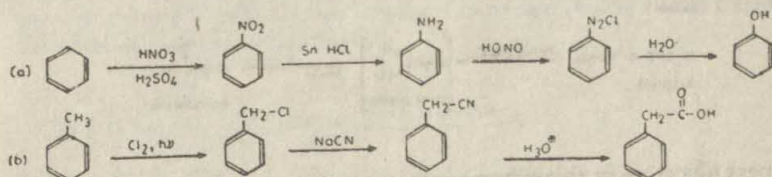
15.2 MODEL SYNTHESIS

We have discussed in the previous section, some of the reactions of functional groups and saw how they could be interconverted. We shall now take a specific case of synthesis in which some of these reactions are employed. Consider the synthesis of a simple alkyl bromide namely, 2-bromo-2-methylbutane starting from 'inorganic materials'.

$$\text{SIMPLE STARTING MATERIALS} \xrightarrow{\ ?\ } \underset{\substack{|\\ CH_3}}{\overset{\substack{Br\\ |}}{CH_3{-}CH_2{-}C{-}CH_3}}$$

2-Bromo-2-methylbutane
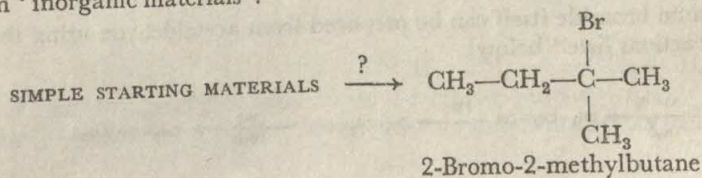
Several routes are possible for the synthesis of this compound. However, we shall indicate one scheme in which a variety of reactions are employed. These transformations are indicated in Scheme 15.5.

$$\underset{\text{Calcium carbide}}{CaC_2} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} \longrightarrow \underset{\text{2-Butanol}}{CH_3-\overset{\overset{OH}{|}}{\underset{|}{C}}-CH_2-CH_3}$$

$$\longrightarrow \underset{\text{2-Bromobutane}}{CH_3-\overset{\overset{Br}{|}}{\underset{|}{C}}-CH_2-CH_3} \longrightarrow \underset{\substack{\text{2-Methylbutanoic}\\\text{acid}}}{CH_3-\overset{\overset{CO_2H}{|}}{\underset{|}{C}}-CH_2-CH_3} \longrightarrow \underset{\text{2-Methyl-I-butanol}}{CH_3-\overset{\overset{CH_2OH}{|}}{\underset{|}{C}}-CH_2-CH_3}$$

$$\longrightarrow \underset{\text{2-Methyl-1-butene}}{CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}=CH_2} \longrightarrow \underset{\text{2-Bromo-2-methylbutane}}{CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{|}{\underset{Br}{C}}}-CH_3}$$
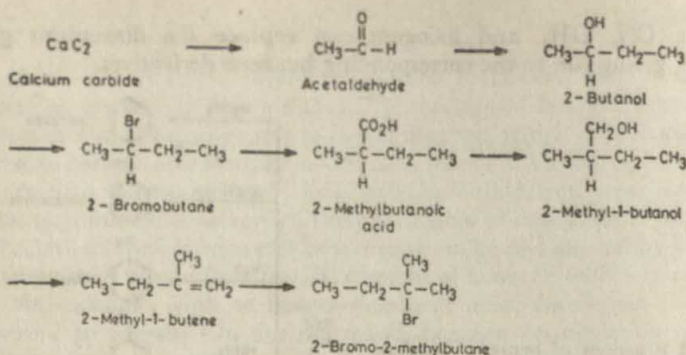
Scheme 15.5   Synthesis of 2-bromo-2-methylbutane

We start our synthesis with calcium carbide (CaC_2), an 'inorganic' compound which is commercially available and employ its reaction with water to give acetylene. Water adds to acetylene in the presence of catalytic amounts of sulphuric acid and mercuric sulphate. The product of addition is an unstable alcohol, namely vinyl alcohol which rearranges to acetaldehyde.

$$\underset{\substack{\text{Calcium}\\\text{carbide}}}{CaC_2} + 2H_2O \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + Ca(OH)_2$$

$$\underset{\text{Acetylene}}{H-C\equiv C-H} + H_2O \xrightarrow{H_2SO_4 \cdot HgSO_4} \left[\underset{\text{Vinyl alcohol}}{CH_2=C\overset{H}{\underset{OH}{\diagdown}}}\right] \rightleftharpoons \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H}$$
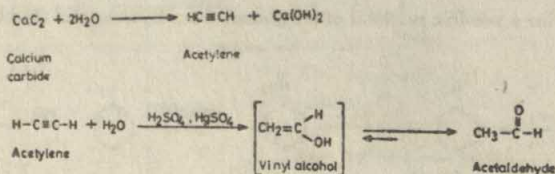
Our next objective in this scheme is to prepare a secondary alcohol namely, 2-butanol utilising acetaldehyde. This can be achieved by the reaction of acetaldehyde with ethyl magnesium bromide (*Grignard reagent*).

$$CH_3-\overset{\overset{O}{\|}}{C}-H + CH_3-CH_2-MgBr \longrightarrow CH_3-\overset{\overset{OMgBr}{|}}{\underset{|}{\underset{H}{C}}}-CH_2-CH_3 \xrightarrow{H_3\overset{\oplus}{O}} \underset{\text{2-Butanol}}{CH_3-\overset{\overset{OH}{|}}{\underset{|}{\underset{H}{C}}}-CH_2-CH_3}$$
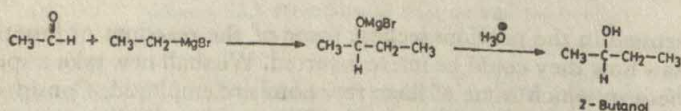
Ethyl magnesium bromide itself can be prepared from acetaldehyde using the sequence of reactions listed below:

$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[H_3\overset{\oplus}{O}]{LiAlH_4} CH_3-CH_2-OH \xrightarrow{PBr_3} CH_3-CH_2-Br \xrightarrow[\text{Ether}]{Mg} CH_3-CH_2-MgBr$$
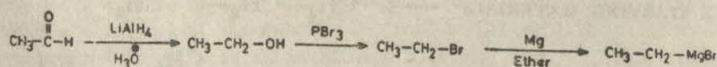
Once having obtained 2-butanol, our next aim is to employ this material in the preparation of 2-methyl-1-butanol, an alcohol containing five carbon atoms. The reactions involved in these transformations are indicated in Scheme 15.6.

$$CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow{PBr_3} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \xrightarrow[Ether]{Mg} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-MgBr$$

$$\xrightarrow{CO_2, H_3O} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CO_2H \xrightarrow{LiAlH_4, H_3O} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH$$
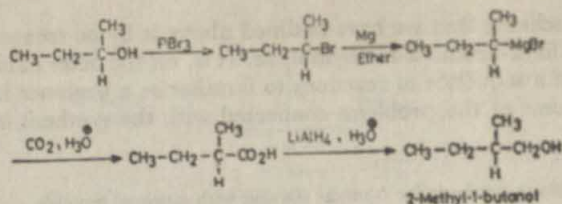
2-Methyl-1-butanol

Scheme 15.6 Formation of 2-methyl-1-butanol from 2-butanol

If we can now bring about the conversion of 2-methyl-1-butanol to 2-methyl-1-butene, then we can obtain the desired final product by the mere addition of hydrogen bromide to this alkene. The dehydration of 2-methyl-1-butanol by the conventional method of treating it with sulphuric acid does not give 2-methyl-1-butene, but gives chiefly 2-pentene, a product formed through the rearrangement of a carbonium ion intermediate.

$$CH_3CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH \xrightarrow[heat]{H_2SO_4} \begin{cases} \rightarrow CH_3-CH_2-CH=CH-CH_3 \\ \qquad\qquad \text{2-Pentene} \\ \rightarrow CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}=CH_2 \\ \qquad \text{2-Methyl-1-butene} \end{cases}$$
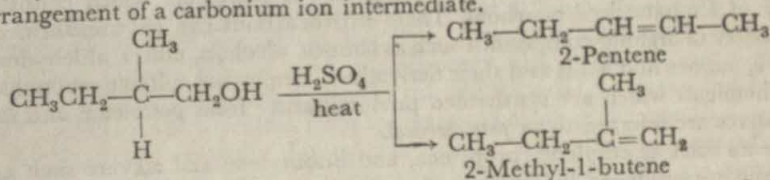
A convenient method of dehydrating 2-methyl-1-butanol is through the pyrolysis of its acetate ester. Treatment of this alcohol with a mixture of acetic anhydride and sodium acetate gives an acetate derivative which when subjected to pyrolysis ($\sim 400°$-$500°C$), undergoes elimination giving rise to 2-methyl-1-butene and acetic acid as products.

$$CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-OH \xrightarrow{(CH_3CO)_2O}$$

$$CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-O-\overset{\overset{O}{||}}{C}-CH_3$$

$$CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-O-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow{\sim 500°}$$

$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}=CH_2 + CH_3-CO_2H$$
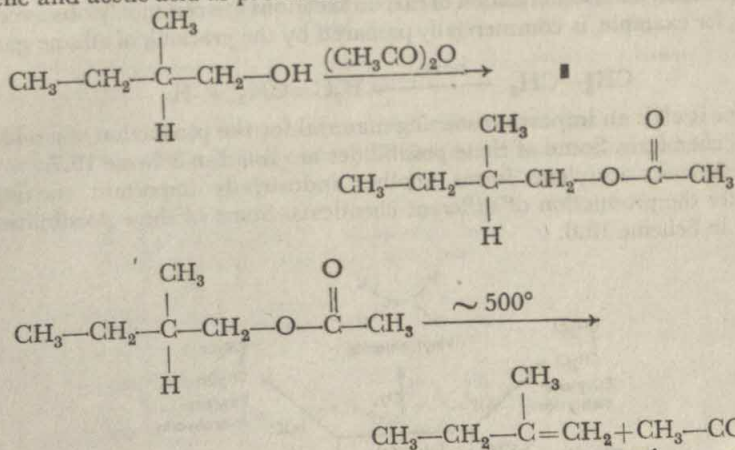
Addition of hydrogen bromide to 2-methyl-1-butene proceeds according to *Markownikoff's rule* (Chapter 14) to give 2-bromo-2-methylbutane.

$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}=CH_2 + HBr \longrightarrow CH_3-CH_2-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

2-Bromo-2-methylbutane
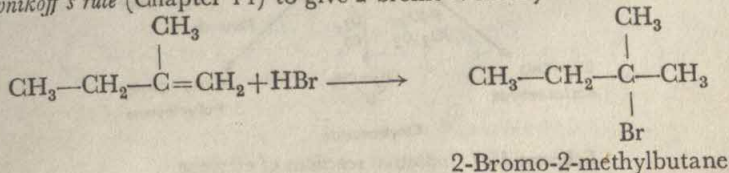
The synthetic scheme that we have outlined above is by no means the most elegant synthesis for 2-bromo-2-methylbutane. It is, on the other hand, merely an elaboration of a sequence of reactions to familiarise a beginner in organic chemistry with some of the problems connected with the synthesis of organic compounds.

Example 15.3 Outline a synthesis for 2-butyne starting with *n*-propyl bromide.

$$CH_3-CH_2-CH_2-Br \xrightarrow{KOH} CH_3-CH=CH_2 \xrightarrow{Br_2} CH_3-CHBr-CH_2-Br \xrightarrow{KOH} CH_3-C\equiv CH$$

$$\xrightarrow{NaNH_2} CH_3-C\equiv C\overset{\ominus\ominus}{N}a \xrightarrow{CH_3I} CH_3-C\equiv C-CH_3 + NaI$$
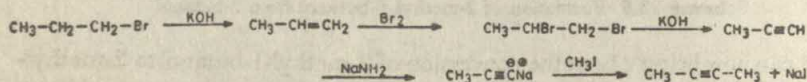
15.3 SYNTHESIS OF CHEMICALS FROM PETROLEUM AND COAL

One of the storehouses of chemicals in nature is petroleum which consists chiefly of aliphatic hydrocarbons. These hydrocarbons can be transformed to a variety of organic compounds such as halides, alcohols, ethers, aldehydes, ketones, amines and acids and their derivatives, employing suitable reactions. The chemicals which are synthesised predominantly from petroleum and its derivatives are referred to as *petrochemicals*.

Alkenes such as ethylene, propylene, and isobutylene and alkynes such as acetylene are produced by thermal or catalytic *cracking* of petroleum hydrocarbons. The catalytic cracking process is generally carried out at 500°–600°C under atmospheric pressure over a suitable catalyst such as manganese, copper, cobalt on a silica-alumina support, or a chromia-alumina catalyst. During the catalytic cracking process, reactions involving the fission of C—C bonds, dehydrogenation and isomerisation of carbon skeletons are commonly observed. Ethylene, for example, is commercially prepared by the cracking of ethane gas.

$$CH_3\text{—}CH_3 \xrightarrow{\text{heat}} H_2C=CH_2 + H_2$$
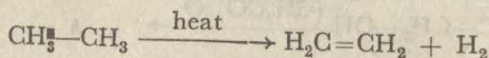
Ethylene itself is an important starting material for the production of a wide variety of chemicals. Some of these possibilities are listed in Scheme 15.7.

Like ethylene, acetylene forms another industrially important starting material for the production of different chemicals. Some of these possibilities are listed in Scheme 15.8.
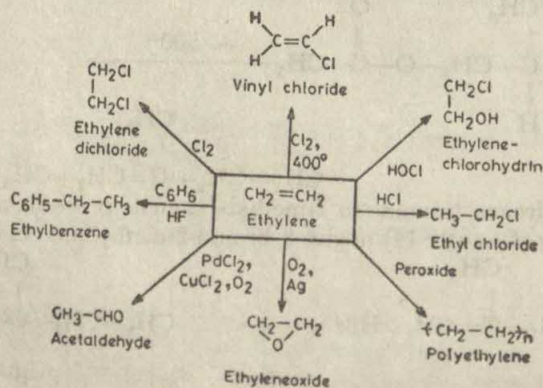
Scheme 15.7 Industrial reactions of ethylene
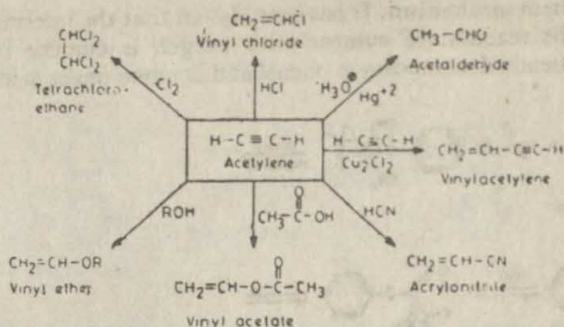
Scheme 15.8 Industrial reactions of acetylene

Catalytic reactions are particularly important in the production of aromatic hydrocarbons from petroleum fractions. Aromatic hydrocarbons such as benzene, toluene, xylenes, and ethylbenzene are produced commercially through such processes. Benzene is the starting material for several industrially useful chemicals as is evident from the reactions listed in Scheme 15.3.

As illustrative examples, let us consider the industrial synthesis of some aromatic compounds such as phenol, phthalic anhydride and certain halogenated aromatic compounds.

Phenol, for example, can be commercially synthesised by different routes. One of the newer methods for the production of phenol, however, is through the

oxidation of isopropylbenzene (cumene). The oxidation is carried out with oxygen in aqueous alkali around 130°C and the reaction proceeds through a

Scheme 15.9 Formation of cumene hydroperoxide

free radical chain mechanism. It has been shown that the intermediate formed initially in the reaction of cumene with oxygen is cumene hydroperoxide which subsequently decomposes to phenol and acetone under acidic conditions.

Cumene hydroperoxide

Scheme 15.10 Decomposition of cumene hydroperoxide

Phenol

Acetone

Another chemical of great commercial importance which is again obtained from aromatic hydrocarbons is phthalic anhydride. Phthalic anhydride is used in the manufacture of polymers, and anthraquinone and other dye intermediates.

Naphthalene

o - Xylene

Phthalic anhydride

Scheme 15.11 Formation of phthalic anhydride

It is known that controlled oxidation of hydrocarbons can yield carboxylic acids. One of the industrial syntheses of phthalic anhydride is by the oxidation of naphthalene (available from coal tar distillates) with air over vanadium pentoxide (V_2O_5) catalyst around 360°–450°C range. Instead of naphthalene, we can start with o-xylene (available from petroleum fractions) which also undergoes a similar oxidation yielding phthalic anhydride (Scheme 15.11).

A third group of compounds of great commercial importance, which are again derived from aromatic hydrocarbons, is the halogenated derivatives. Some of these polyhalogenated derivatives find considerable use as *insecticides*. The remarkably active insecticides DDT (dichlorodiphenyltrichloroethane) and gammexane (γ-isomer of benzene hexachloride) are examples of this group of compounds.

DDT is commercially prepared by the reaction of chloral hydrate (hydrated form of trichloroacetaldehyde) with chlorobenzene in the presence of sulphuric acid. DDT has shown spectacular success in the control of diseases like malaria which are transmitted by mosquitos, and also for protecting crops against a

variety of pests. In recent years, however, doubts have been raised about the harmful effects of DDT to human and animal species, thereby discouraging the use of DDT in, at least industrially advanced countries.

Chlorobenzene   Chloral hydrate   DDT

Gammexane, which is one of the six isomers of benzene hexachloride, is formed by the photochemical addition of chlorine to benzene.

γ-Isomer of benzene hexachloride
(Gammexane)

Another commercially useful starting material for organic chemicals is coal (or other carbonaceous materials). One of the methods of producing parafins from carbonaceous materials is the *Fischer-Tropsch process*, which employs the hydrogenation of water gas ($CO + H_2$) in presence of suitable catalysts. Water gas is a mixture of carbon monoxide and hydrogen formed by treating coke with steam at high temperatures.

$$C + H_2O \rightarrow \underbrace{CO + H_2}_{\text{Water gas}}$$
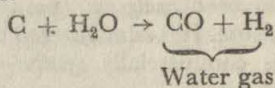
Hydrogen is added to water gas in appropriate ratios and the mixture is heated under pressure over a cobalt catalyst. The reaction is assumed to proceed through the formation of cobalt carbide (CoC) which ultimately is converted to the hydrocarbon and cobalt metal (regeneration of the catalyst). Both alkanes and alkenes are formed under the Fischer-Tropsch conditions.

$$n CO + 2n H_2 \xrightarrow{\text{Catalyst}} \underset{\text{Alkene}}{C_n H_{2n} + n H_2 O}$$

$$n CO + (2n+1) H_2 \xrightarrow{\text{Catalyst}} \underset{\text{Alkane}}{C_n H_{2n+2} + n H_2 O}$$
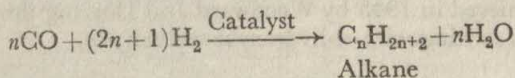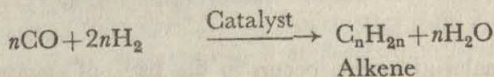
Several by-products such as alcohols, aldehydes, ketones and carboxylic acids are also formed in the *Fischer-Tropsch* reaction. It is possible to modify the reaction conditions in such a way as to give better yields of these by-products, if so desired.

Example 15.4 Suggest a feasible industrial synthesis of (*a*)*t*-butyl chloride from isobutylene,

(b) cyclohexanone from cyclohexane, (c) isopropyl alcohol from propene, (d) ethylene glycol from ethylene, and (e) p-chlorotoluene from toluene.
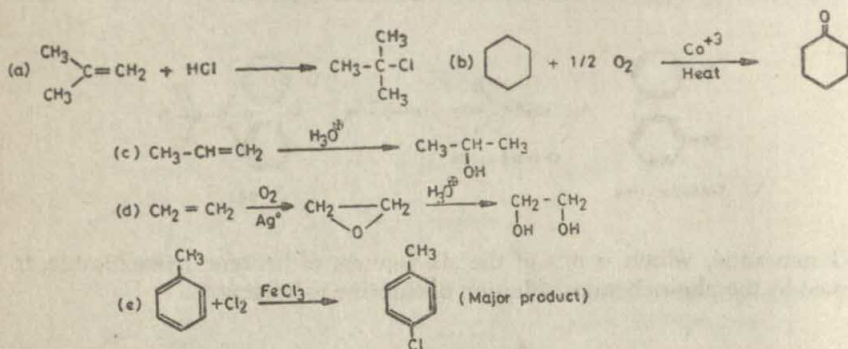
15.4 SYNTHESIS OF PHYSIOLOGICALLY USEFUL COMPOUNDS

There are numerous organic compounds which have specific physiological activity and consequently they can be used as drugs in curing different diseases. One of the major concerns of a synthetic organic chemist is to devise ways and means of synthesising newer compounds of different structural features and to test the physiological activity of these compounds. We are already well acquainted with the use of common medicines such as aspirin, quinine, penicillin, and tetracyclin. We shall now briefly examine the synthesis of a few representative examples of physiologically active compounds.

15.4.1 Acetylsalicylic Acid (Aspirin)

One of the most commonly used *analgesics* (pain killers) is acetylsalicyclic acid, commonly known as *aspirin*. It is administered as its water-soluble sodium salt. Acetylsalicylic acid is commercially synthesised by the acetylation of salicylic acid with acetic anhydride.
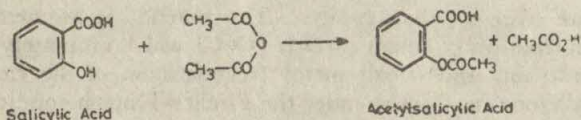
15.4.2 Quinine

Quinine, an antimalarial agent, occurs in the bark of *cinchona* trees and its synthesis was achieved in 1945 by Woodward and Doering through a series of several reactions, starting with m-hydroxybenzaldehyde.
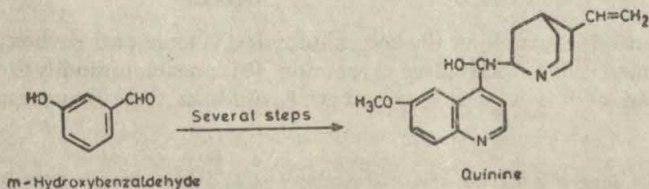
15.4.3 Penicillin

One of the most remarkable *antibiotics* which has revolutionised modern medicine is *penicillin*, produced from the mould *Penicillium notatum*. There are at least five naturally occurring penicillins, each containing the same gross structural features (a β-lactam fused to a thiazolidine ring). One of the penicillins, namely penicillin V, was synthesised by Sheehan and Henry-Logan (1959) by using pencillamine as the intermediate. Pencillamine itself has been synthesised through a series of reactions starting with *dl*-valine.
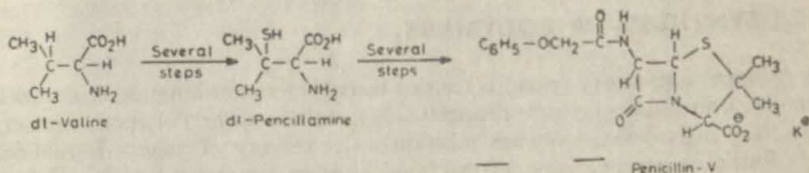
15.4.4 Vitamin A

The collective name *vitamin·A* is given to a mixture of compounds consisting of vitamin A_1 and vitamin A_2, differing only in two hydrogen atoms. Vitamin A plays an important role in the chemistry of the process of vision by being a
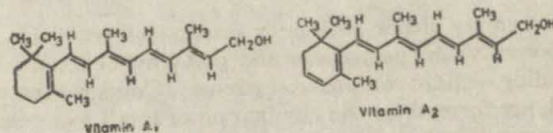
source of retinene. *Retinene* is an aldehyde formed through the oxidation of vitamin A by the coenzyme, *nicotinamide adenine nucleotide* (NAD⁺) in conjunction with the enzyme, *alcohol dehydrogenate* (ADH).
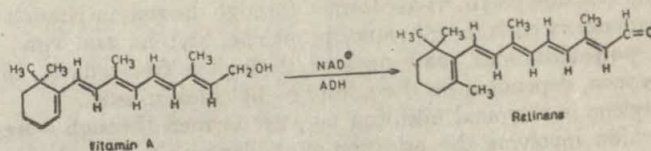
Vitamin A_1 is found in large amounts in the liver of salt-water fish, whereas vitamin A_2 is found in the liver of fresh-water fish. Besides, a number of naturally occurring compounds such as β-carotene (from carrots) possessing the skeletal structure of vitamin A_1 are converted to vitamin A_2 in the human body.

Vitamin A_1 has been synthesised in the laboratory by different groups of workers. One of these, due to Isler and co-workers (1911), starts with β-ionone, a compound which had been synthesised earlier.

The importance of vitamins is discussed in Chapter 18.
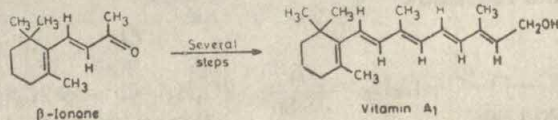
Example 15.5 Write equations illustrating the synthesis of aspirin from benzene.

Aspirin
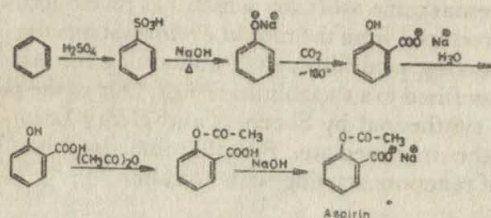
15.5 SYNTHESIS OF POLYMERS

A *polymeric compound* (*polymer*) is formed through the combination of numerous smaller units (*monomers*) by appropriate chemical reactions. Polymers, in general, are very high molecular-mass substances. A variety of polymeric materials are found in nature. Some of the familiar organic materials such as starch, cellulose, proteins (polypeptides), and natural rubber are all polymeric compounds. Since the beginning of this century, there has been tremendous activity in the area of polymer chemistry, primarily with a view to producing different synthetic polymers of very specific chemical and physical properties. Today, the polymer industry is one of the major chemical industries in any advanced country.

Polymers are formed by either *addition* or *condensation* reactions. Addition polymers such as polyethylene, polystyrene and polyvinyl chloride are formed from the corresponding olefinic compounds (alkenes). Condensation polymers, on the other hand, are formed by the elimination of small molecules such as water, alcohol and ammonia in the reaction of polyfunctional, monomeric units. Polyesters and polyamides are examples of condensation polymers.

15.5.1 Addition Polymers

Most of the addition polymers are formed through the polymerisation of simple olefinic monomers such as ethylene, propylene, styrene and vinyl chloride. Addition polymerisations may proceed through a free-radical, cationic or anionic process, depending on the nature of the catalyst used.

Polyethylene is a typical addition polymer formed through a free radical chain reaction involving the addition of ethylene units. The first step in this reaction is the production of free radicals and this is achieved by the thermal decomposition of an initiator like peroxide. Benzoyl peroxide or di-*t*-butylper-

$$CH_2=CH_2 \xrightarrow[\text{(Peroxide)}]{\text{Catalyst}} \{CH_2-CH_2\}_n$$

Ethylene   Polyethylene
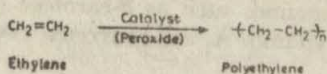
oxide generally serves as the initiator. The thermal decomposition of benzoyl peroxide, for example, gives rise to the benzoyloxy radical which can subseqently decompose to phenyl radical and carbon dioxide.

Chain initiation reactions

$$\underset{\text{Benzoyl peorxide}}{C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5} \xrightarrow{\underset{70-80°}{\Delta}} \underset{\text{Benzoyloxyradical}}{2C_6H_5-\overset{O}{\overset{\|}{C}}\cdot} \longrightarrow 2C_6H_5\cdot + 2CO_2$$
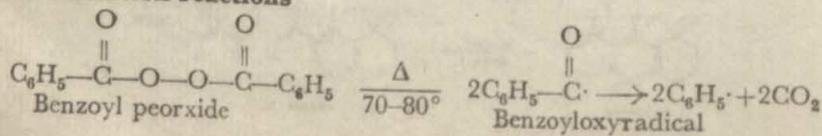
Chain propagation reactions: Addition of initiator radicals to ethylene or other monomeric species gives rise to a new radical species which can subsequently react with successive molecules of the monomer units to give a polymeric chain.

$$C_6H_5 \cdot + CH_2=CH_2 \rightarrow C_6H_5-CH_2-CH_2 \cdot \xrightarrow{CH_2=CH_2}$$
$$C_6H_5-CH_2-CH_2-CH_2-CH_2 \cdot \rightarrow C_6H_5-(CH_2-CH_2)_n-CH_2-CH_2$$
$$\text{Polymeric chain}$$
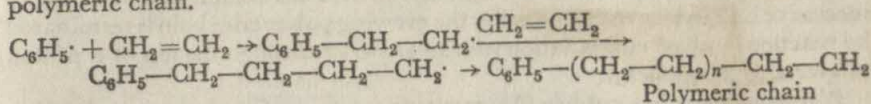
Chain termination reactions: The process of addition of monomeric units to the growing polymer chain can be interrupted by any one of the chain termination reactions, such as the combination of two radical chains (radical recombination), a disproportionation reaction or by combination with any other species which inhibit the further production of radical chain (inhibitors). Substances such as quinones and amines are commonly used inhibitors.

$$C_6H_5-(CH_2-CH_2)_n-CH_2-CH_2 \cdot + \cdot H_2C-H_2C-(CH_2-CH_2)_n-C_6H_5$$
$$\xrightarrow{\text{Radical combination}} C_6H_5-(CH_2-CH_2)_{2n+2}-C_6H_5$$

$$C_6H_5-(CH_2-CH_2)_n-CH_2-CH_2 \cdot + InH \rightarrow$$
$$C_6H_5-(CH_2-CH_2)_n-CH_2-CH_3 + In \cdot \text{ (Inhibitor)}$$
$$In \cdot + In \cdot \rightarrow \text{Inert Products}$$
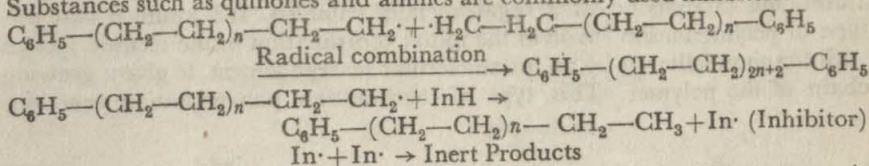
Polyethylene produced in this manner has about 800 to 1000 monomeric ethylene units and possesses properties characteristic of plastics. It is tough flexible, water-resistant and can be moulded into useful articles.

15.5.2 Ionic Addition Polymerisation

Ionic catalysts can bring about the polymerisation of olefinic monomers, just as in free-radical polymerisation reactions. Isobutylene, for example, can be

polymerised by the addition of small amounts of sulphuric acid. The reaction is initiated by the formation of a carbonium ion, caused by the addition of a proton to isobutylene. The propagation of the polymerisation reaction is through a process by which the initially formed carbonium ion adds on to successive isobutylene units. Finally, the growing polymeric chain is terminated by reactions such as combination with an anion or through the loss of a proton to give a terminal olefin.

Polyisobutylene has rubber-like properties and is referred to as *butyl rubber*. It is used in the manufacture of cycle tubes and other useful items.

15.5.3 Coordination Polymerisation

In recent years, another mode of addition polymerisation, involving organo-metallic catalysts has gained considerable importance. Most monomeric compounds of the type $R—CH=CH_2$ can be polymerised by titanium-aluminium catalysts or other organometallic catalysts. It is assumed that this type of polymerisation involves the initial coordination of the olefinic species with titanium followed by an intramolecular rearrangement, to give a growing chain of the polymer. This type of coordination polymerisation reactions
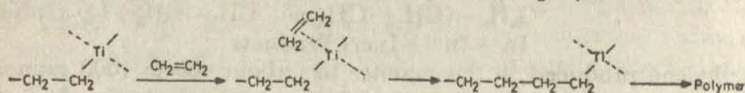
have been studied through the pioneering investigations of Ziegler and Natta. The organometallic catalysts used are thus known as Ziegler-Natta catalysts.

Example 15.6 Explain the following terms: (*a*) isotactic polymer, (*b*) syndiotactic polymer, and (*c*) atactic polymer.

When a substituted vinyl monomer $(CH_2=CHR)$ is polymerised, the carbon atom bearing the substituent becomes asymmetric and may take three possible arrangements. In most free radical polymerisations, a random arrangement is produced, and the polymer is *atactic*. If all the asymmetric carbon atoms have the same configuration with respect to each other, the polymer is *isotactic*. When the configuration alternates, it is *syndiotactic*. Isotactic and syndiotactic polymers are obtained usually with Zeigler-Natta catalysts.
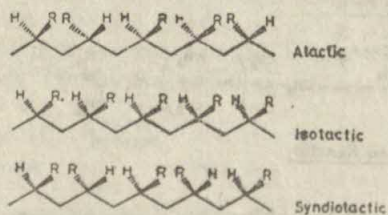
15.5.4 Copolymerimisation Reaction

A *copolymer* is a polymeric material containing two different recurring monomeric species. The amount of each kind of monomer incorporated depends on the concentration of the monomer at any given time and also its reactivity towards the growing radical chain. Copolymerisation of 1,3-butadiene and styrene gives a *synthetic rubber* substitute for natural rubber. Natural rubber itself is a polymer of 2-methyl-1,3-butadiene (or isoprene).
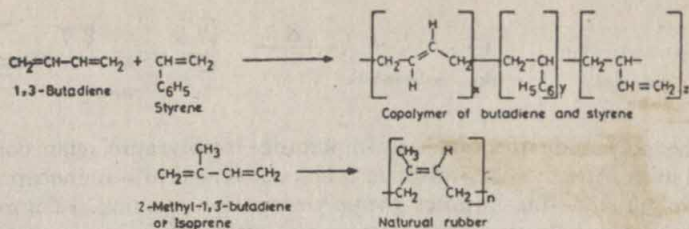
The hardness and durability of both natural and synthetic rubbers are improved by a technique known as *vulcanization*. During vulcanization, rubber is heated with sulphur which cross links different polymeric chains through
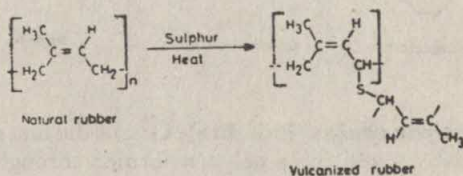
sulphur linkages thereby rendering hardness to the polymer. The vulcanized rubber is used in the manufacture of motor tyres and allied articles.

15.5.5 Synthesis of Condensation Polymers

Condensation polymers are those formed by the combination of different monomeric units through the loss of small molecules such as water, alcohol, or ammonia. Polyesters (e.g. Dacron), polyamides (e.g. Nylon), phenol-formaldehyde resin (e.g. Bakelite) are all examples of condensation polymers.

Polyesters: Polyethylene terephthalate is one of the important polyesters that is commercially manufactured. Fibres such as *dacron* and *terylene* are made from this polymer. Polyethylene terephthalate is manufactured by an ester-exchange reaction between dimethyl terephthalate and ethylene glycol. This reaction is facilitated by the addition of weak basic catalysts such as calcium acetate or other salts of carboxylic acids.

Polyethylene terephthalate
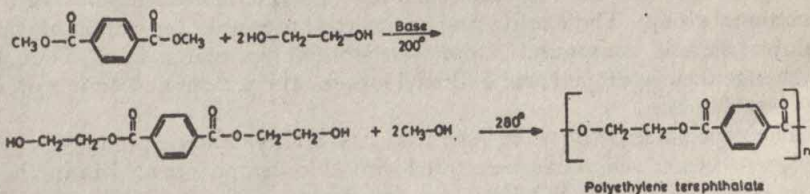
Polyamides: Polyamides are prepared from the reaction of a dicarboxylic acid with a diamine. *Nylon* (66) or polyhexamethylene adipamide is one of the best known polyamides. This polymer is prepared by the condensation of adipic acid with hexamethylenediamine. Nylon is a polymer with high tensile strength and can be converted into fibres or moulded into articles.

$$HO_2C-(CH_2)_4-CO_2H \quad + \quad H_2N-(CH_2)_6-NH_2 \quad \xrightarrow{\Delta} \quad \left[\begin{matrix} H & O \\ | & || \\ N-C-(CH_2)_4-C-N-(CH_2)_6 \\ & & | & | \\ & & O & H \end{matrix} \right]_n + H_2O$$

Adipic acid   Hexamethylenediamine   Nylon
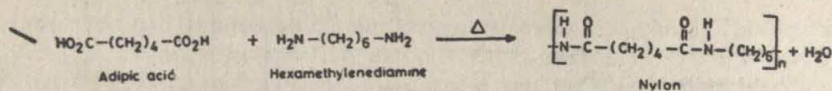
Another polyamide of commercial importance is polycaprolactam commonly referred to as *Nylon 6*. ε-Caprolactam is first converted to ε-aminocaproic acid by hydrolysis and this initiates the polymerisation reaction. ε-Caprolactam itself is commercially prepared from cyclohexane through a photochemical reaction (see, under photochemical synthesis in section 15.6).

$$\text{ε-Caprolactam} \quad \xrightarrow{H_2O} \quad HO_2C-(CH_2)_5-NH_2 \quad \xrightarrow[\Delta]{(-H_2O)} \quad \left[(CH_2)_5-\underset{\underset{O}{||}}{C}-\underset{\underset{H}{|}}{N} \right]_n$$

ε-Caprolactam   ε-Aminocaproic acid   Nylon-6
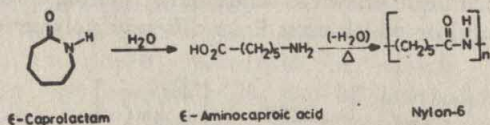
Phenol-formaldehyde resins (Bakelite): One of the first synthetic polymers to be prepared is *Bakelite* which is a polymer formed through the condensation of phenol and formaldehyde. The reaction of phenol with excess of formaldehyde in the presence of a basic catalyst gives a polymeric product containing phenol moieties linked in the *ortho-* and *para-*positions by methylene groups.

Phenol + CH$_2$O (Formaldehyde) → Phenol-formaldehyde resin
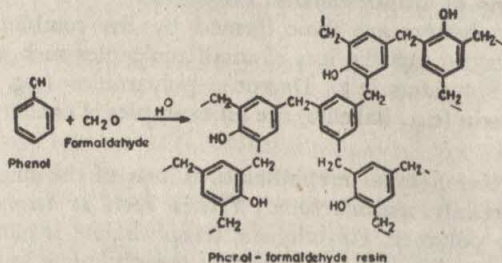
15.5.6 Ion-exchange Resins

Ion-exchange resins are high molecular mass polymeric materials having ionic functional groups. These resins find commercial use in the separation of water-soluble organic compounds from water-soluble inorganic salts. They can exchange their hydrogen and hydroxyl ions for the cations and anions present in the solution.

The copolymerisation of styrene with 1, 4-divinylbenzene produces a polystyrene polymer which can be treated with chlorosulphonic acid to introduce sulphonic acid groups (SO_3H) in the *para*-positions of the phenyl groups. The sulphonated polymer is a *cation-exchange resin* and is useful for the softening of hard water. When hard water containing calcium salts is allowed to percolate through a bed of this cation-exchange resin (sodium salt), the calcium ions are exchanged for the sodium ions. The calcium ions from the resin can be later replaced to regenerate the resin by passing a solution of sodium chloride over the resin.

CH=CH₂ + CH=CH₂ / CH₂=NC

Styrene   1,4-Divinylbenzene →

1. ClSO₃H
2. NaOH

Copolymer

R = SO₃⁻ Na

Cation-exchange resin
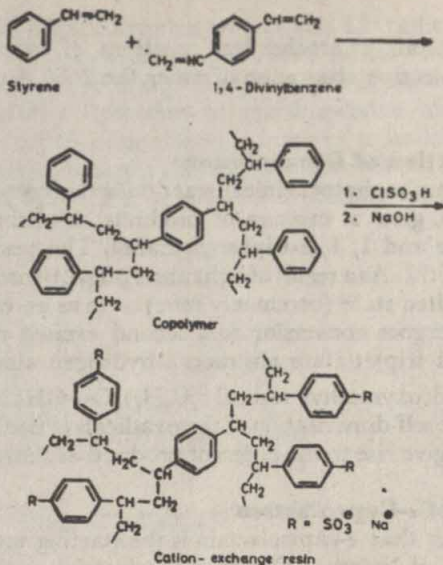
Anion-exchange resins containing appropriate functional groups can be prepared in a similar manner from suitable starting materials.

15.6 PHOTOCHEMICAL SYNTHESIS

Photochemical reactions are those which are caused by the absorption of light (see Chapter 13). In nature we have several examples of photochemical reactions. Photosynthesis of sugars in plants, for example, involves the reaction between carbon dioxide and water (Chapter 18). This reaction is sensitised (an energy-transfer mechanism) by *chlorophyll*, the green pigment present in the leaves and stems of plants.

$$6CO_2 + 6H_2O \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} C_6H_{12}O_6 + 6O_2$$
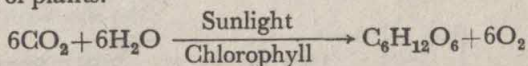
In this section, we shall examine a few simple photochemical reactions and their applications to the synthesis of organic molecules.

Most of the photochemical reactions are brought about by the absorption of visible and ultraviolet light. The photon energies associated with these radiations vary from 38 (corresponding to photons of wavelength 7500 A) to 71 kcal mol⁻¹ (4000 A) for visible light and 71 to 143 kcal mol⁻¹ (2000 A) for ultraviolet light. Absorption of light causes excitation of electrons in molecules to higher-energy molecular orbitals, thereby producing excited state species. The visible and ultraviolet spectra of any molecule are therefore indicative of the type of energy absorptions that can occur in that molecule. The absorption spectrum of benzophenone, C_6H_5—CO—C_6H_5, for example, shows two maxima at 2450 A and 3450 A respectively. Of these, the band at 3450 A is lower in intensity and is assigned to a transition, in which an electron from a non-bonding atomic orbital at oxygen is promoted to an antibonding π^* orbital of the carbonyl group. Similarly, the band at 2450 A is assigned to a $\pi-\pi^*$ transition wherein an electron from a bonding π orbital of the aromatic species is promoted to an

antibonding π^* orbital. Photochemical reactions of benzophenone can be controlled by the selective absorption of either the 2450 A or the 3450 A radiation.

15.6.1 Photoreduction of Benzophenone

An example of a simple photochemical reaction is the reduction of benzophenone in toluene to give a mixture of products consisting of benzpinacol, 1, 2-diphenylethane and 1, 1, 2-triphenylethanol. The reaction sequences are shown in Scheme 15.12. As a result of light absorption, benzophenone is initially converted to an excited state (commonly referred to as an excited singlet state) which rapidly undergoes conversion to a second excited triplet state (triplet state). This excited triplet state abstracts a hydrogen atom from toluene to give a diphenylhydroxymethyl radical $(C_6H_5)_2\dot{C}$—OH) and benzyl radical $(C_6H_5$—$CH_2{}^{\cdot})$. The self dimerisation of these radicals or combination of the two radical species will give rise to the different products as shown in Scheme 15.12.

15.6.2 Synthesis of ε-Caprolactam

We have seen earlier that ε-captrolactam is the starting material for the commercial production of Nylon-6. One of the industrial methods for the manufacture of ε-caprolactam is a process which utilises cyclohexane. In this process cyclohexane is first converted to nitrosocyclohexane through a photochemical reaction involving its treatment with nitrosyl chloride (ONCl). As a result of
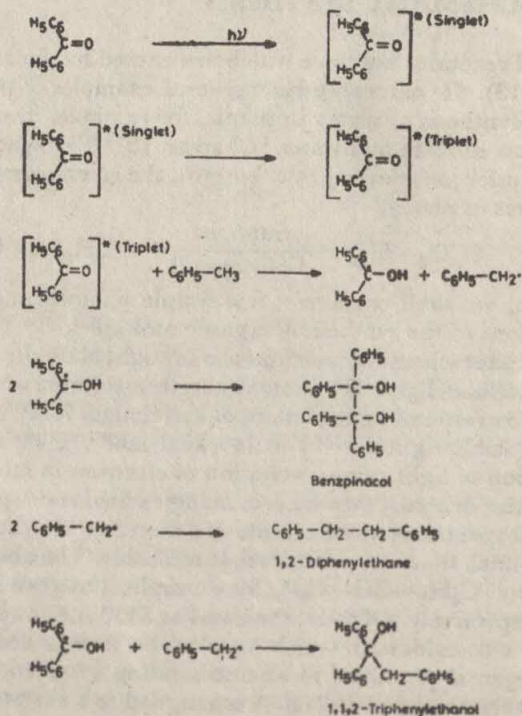
Scheme 15.12 Photoreduction of benzophenone

light absorption, NOCl is converted to ·NO and Cl· radicals. Abstraction of a hydrogen atom from cyclohexane by chlorine radical will give a cyclohexyl radical. Combination of cyclohexyl radical with ·NO radical gives nitrosocyclohexane which readily isomerises to cyclohexanone oxime. Conversion of cyclohexanone oxime to ε-caprolactam involves a molecular rearrangement (*Beckmann rearrangement*) brought about by treatment of the oxime with sulphuric acid in presence of water. The details of this reaction are indicated in Scheme 15.13.

Cyclohexanone oxime
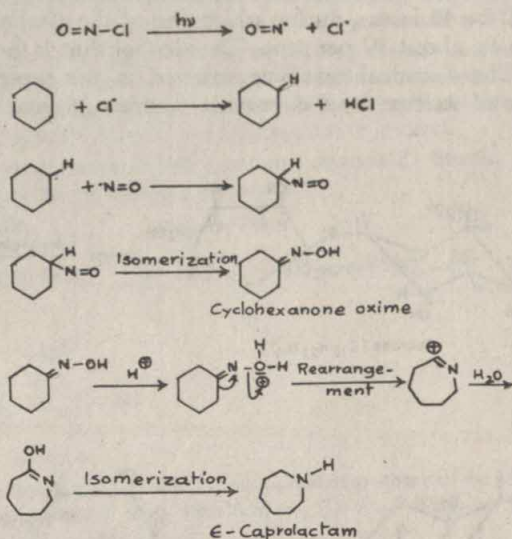
ε - Caprolactam

Scheme 15.13 Formation of ε-caprolactam from cyclohexane

Example 15.7 How can photochlorination of toluene be used in the synthesis of benzyl alcohol, benzaldehyde and benzoic acid?
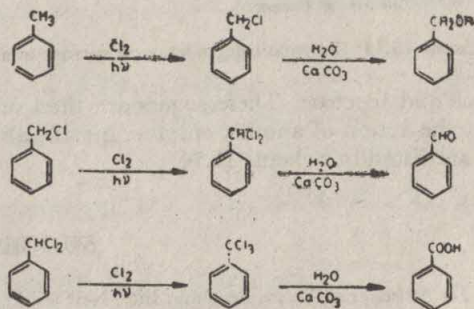
15.7 ENZYMATIC SYNTHESIS

Several organic transformations are very elegantly brought about by the specific action of enzymes (see Chapters 13 and 18 for more details about

enzymes) which are biological catalysts. One of the earliest known enzymatic reactions is the fermentation of starch and sugars to produce alcohol. *Molasses*, for example, can be fermented to ethyl alcohol by the addition of *yeast* under controlled conditions.

Molasses contains a mixture of sucrose (cane sugar), glucose and fructose. The commercial production of ethyl alcohol from molasses involves the fermentation of a solution of molasses maintained around pH 4–5 by the addition of a small amount of yeast. The reaction mixture is normally kept around 25°–30°C for 45 hours, during which period the alcohol concentration slowly builds up to about 10 per cent. The alcohol that is formed is purified by distillation. The chemical reactions involved in the process include, the initial hydrolysis of surcose by the enzyme *invertase* present in yeast, to a
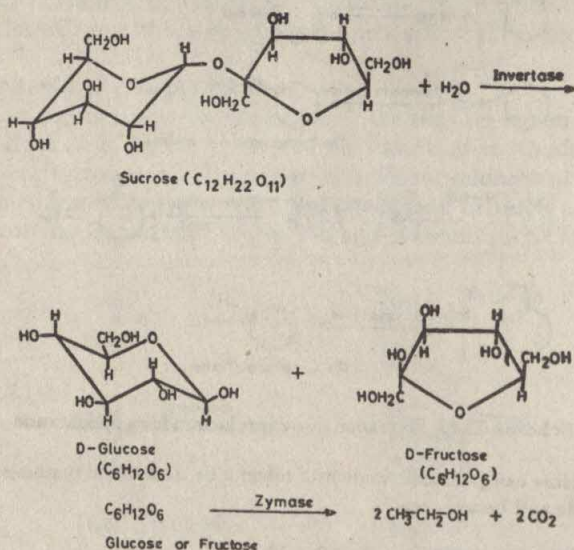
Scheme 15.14 Enzymatic degradation of sucrose to alcohol

mixture of glucose and fructose. These sugars are then subsequently converted to ethanol by the action of another enzyme, *zymase*, also present in yeast. These reactions are listed in Scheme 15.14.

SUGGESTED READING

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J. B. HENDRICKSON, D. J. CRAM and G. S. HAMMOND, *Organic Chemistry*, McGraw-Hill Book Co., New York, 1970.

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PROBLEMS

15.1 Indicate the reagent(s) needed to bring about the following functional group conversions: (a) –CHO to –CH$_2$OH, (b) –CN to –COOH, (c) –NO$_2$ to –NH$_2$, (d) –COOH to –COCl, and (e) $>$CHOH to $>$C=O.

15.2 Write equations showing how each of the following compounds could be synthesised from acetic acid: (a) ethanol, (b) ethyl acetate, (c) diethylamine, (d) *n*-propylamine, and (e) *n*-propanoic acid.

15.3 Starting from ethanol, how would you synthesise the following compounds? (a) *n*-propyl alcohol, (b) diethyl ether, (c) methyl propionate, and (d) ethyl amine.

15.4 Show by means of equations, methods for affecting the following using no other organic materials than those given. Indicate all important reagents and catalysts: (a) 1-propanol to 2-bromopropane, (b) *n*-butyl alcohol to methyl ethyl ketone, (c) acetaldehyde to 2-methyl-2-butanol, and (d) propylene to glycerol.

15.5 How do nucleophiles react with a carbonyl compound? Starting from acetone how would you prepare the following compounds?

$$\begin{matrix} & \underset{|}{\overset{CH_3}{|}} \\ (a) & CH_3-CH-NH_2, \end{matrix} \quad \begin{matrix} & \underset{|}{\overset{CH_3}{|}} \\ (b) & CH_3-\underset{|}{C}-OH, \\ & CH_3 \end{matrix} \quad \begin{matrix} & \overset{CH_3}{|} \\ (c) & CH_3-CH-CH_2-Br, \end{matrix}$$

$$\begin{matrix} & \overset{H_3C}{|} \\ (d) & CH_3-C-C-OH \\ & \underset{HO}{|} \; \underset{O}{\|} \end{matrix}$$
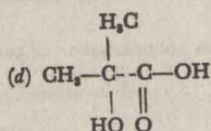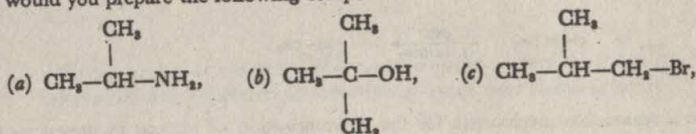
15.6 Outline all steps in a possible industrial method of synthesis of the following compounds starting from acetylene: (a) acetaldehyde, (b) vinyl chloride, (c) ethylene glycol, (d) propyne, and (e) ethanol.

15.7 Suggest a series of reactions which could be used for the following conversions: (a) benzyl alcohol into benzyl benzoate, and (b) benzene into benzylamine.

15.8 Outline the syntheses of the following compounds starting from benzene and any other organic compound containing one or two carbon atoms. Inorganic reagents may be used: (a) acetophenone, (b) β–phenylethanol, (c) benzoic acid, and (d) benzylamine.

15.9 Write out structures of compounds *A* to *F* in the synthetic scheme shown below:

$$CH_3-CH_2-OH \xrightarrow{PBr_3} A \xrightarrow[Ether]{Mg} B \xrightarrow[H_3O]{CO_2} C \xrightarrow[H_3O]{LiAlH_4} D \xrightarrow[heat]{H_2SO_4} E \xrightarrow[(Peroxide)]{HBr}$$
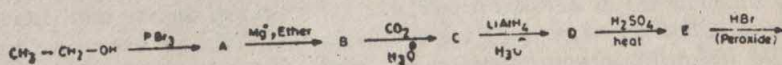
15.10 Show how 4-methyl-3-hexanone $\left(CH_3-CH_2-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3\right)$ may be synthesised from ethyl propionate $\left(CH_3-CH_2-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_3\right)$.

15.11 Give a reasonable scheme for the manufacture of each material from stated starting material: (a) diethyl ether from ethylene, (b) acetone from propene, (c) ethyl acetate from ethanol, (d) benzaldehyde from benzene, (e) dichloromethane from methane (f) 2, 4, 6-trinitrotoluene from benzene, (g) benzyl alcohol from benzene, and (h) aniline from benzene.

15.12 Indicate the reaction mechanism to show how each of the following reactions used in chemical industry occurs.

(a) $+ CH_3-CH = CH_2$ $\xrightarrow{H_2SO_4}$

(b) $\begin{array}{c} CH_3 \\ C=CH_2 \\ CH_3 \end{array}$ $+$ $\begin{array}{c} CH_3-CH-CH_3 \\ CH_3 \end{array}$ $\xrightarrow{H_2SO_4}$ $CH_3-CH-CH_2-\overset{\underset{CH_3}{|}}{\underset{CH_3}{\overset{CH_3}{|}}}C-CH_3$

(c) $CH_3-CH=CH_2$ $+$ Cl_2 $\xrightarrow{500°}$ $CH_2=CH-CH_2-Cl$

(d) $+$ $NaOH$ $+$ CO_2 $\xrightarrow{H_3O^{\oplus}}$

(e) $CH_2=CH_2$ $\xrightarrow[\text{2. Ca(OH)}_2]{\text{1. HOCl}}$ $\overset{CH_2-CH_2}{\underset{O}{\diagdown\diagup}}$
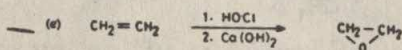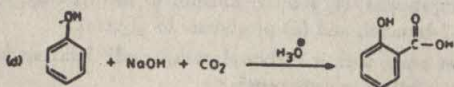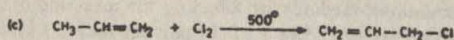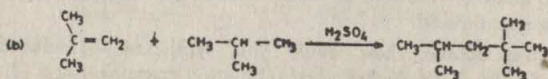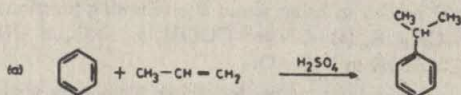
15.13 Give a reasonable mechanism for the polymerisation of styrene in presence of butyl lithium catalyst.

15.14 Which of the following polymers are made by addition polymerisation or condensation polymerisation, and also name the monomer (s): (a) teflon, (b) nylon, (c) plexiglass, (d) orlon, and (e) saran.

16
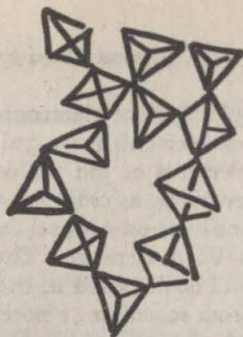
Chemistry of Representative Elements and Noble Gases

The members of the same group of elements (arranged as every eighth in a group) stand to each other in the same relation as the extremities of one or more octaves in music.

JOHN NEWLANDS

The properties of elements were periodic functions of their atomic weights.
There is an element as yet undiscovered, I have named it eka-aluminium. By properties similar to those of the metal aluminium you shall identify it. Seek it, and it will be found.

DMITRI MENDELEEF

When Mendeleef classified elements in a periodic table, it was on the basis of the regularities observed in the physical and chemical properties of various elements. We have seen how the quantum theory of atomic structure has given a proper meaning and justification to this periodic classification of elements into various groups and rows. The properties of the elements in a given group are expected to be similar, since they show similarities in their electronic configurations, and chemistry is predominantly controlled by the configuration of electrons in atoms. We shall study in this chapter the properties of some representative groups of elements. The chemistry of carbon compounds, known as organic chemistry, was discussed in the previous two chapters. The chemistry of the rest of the elements is known as *inorganic chemistry*, and shall be of our concern now.

A look at group I of the periodic table shows that in the elements belonging to this group, the outermost electronic level possesses a single s electron. The chemical properties of the elements of the I group are thus a direct consequence of this single valence electron. Similarly, the alkaline earth metals of group II have similar properties due to the presence of two s electrons in their outermost shells. The elements of groups IIIA, IVA, VA, VIA and VIIA have partially filled p orbitals in their outermost shells. When we come to group

513

VIII, we notice all the elements in this group have completely filled electronic levels. As a consequence, the chemical reactivity of these elements is insignificant, and these elements are referred to as the inert elements or the 'noble elements' or since they are all gases at ordinary temperatures, as *noble gases*. The element hydrogen, due to the existence of only one electron around its nucleus exhibits properties similar to groups IA and VIIA elements. The chemistry of representative elements of various groups will be discussed in this chapter. When we turn to the nine elements starting from scandium, a noteworthy fact is that electrons are progressively filled in the $3d$ levels, while the $4s$ level is already filled. These elements, with the same outer electron configuration, but varying $3d$ electron populations are termed the $3d$ *transition elements* and they will be of our concern in Chapter 17.

16.1 GROUP IA ELEMENTS: ALKALI METALS

The alkali metals include lithium, sodium, potassium, rubidium, cesium and francium. The elements of this sub-group immediately follow the helium family (noble gases) in the periodic system. They have remarkably similar properties and display some interesting trends in chemical behaviour.

16.1.1 General Characteristics

Alkali metals have bright lustre when freshly cut and are excellent conductors of heat and electricity. They are soft and malleable and have low melting points. The softness, low densities and the relatively low melting points indicate that the interatomic bonds in all alkali metals are weak. The relative weakness of the interatomic bond in these metals can be assessed from the heat of atomisation* of the metals (ΔH_{atom}) which is a direct measure of the strength of metallic bond. For alkali metals the values of ΔH_{atom} listed in Table 16.1 show that with the increase in the size of the metal atom, the metallic bond strength decreases. Generally, increasing atomic size progressively weakens intermolecular bonds. Therefore, softness increases while the melting and boiling points decrease in the group from lithium to cesium. The greatest difference in melting and boiling points for two consecutive members of the family is between lithium and sodium. This we should expect from the sizes and the electronic configurations of these elements. A significant difference between lithium and other alkali metals is that whereas in lithium the valence electron in the outermost shell comes after s^2 electron configuration, in the other metals the valence electron is after s^2p^6 configuration.

The ionisation energy (IE) of the elements, which is a function of the effective nuclear charge and size, decreases down the group (Table 16.1). The effective nuclear charge in these cases is approximately constant due to the completed $(n-1)s^2(n-1)p^6$ shell and therefore, IEs are inversely proportional to the atomic radius. Thus, lithium has the highest and cesium the lowest ionisation energy. The atomic and ionic sizes and the ionisation energies provide a basis for explaining the trends in many of the properties of the alkali metals and their compounds.

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*It represents the energy required to transform one mole of crystalline metal at 25°C and 1 atm to 1 mole of gaseous atom [$M(s) \rightarrow M(g)$].

Table 16.1 Physical Properties of the Group IA Elements(a)

Property		Lithium	Sodium	Potassium	Rubidium	Cesium
				Element		
Atomic mass		6·94	22·99	39·10	85·47	132·90
Atomic number		3	11	19	37	55
Isotopes		6, 7	22, 23	39, 40, 41	85, 87	133
Electronic structure		He $2s^1$	Ne $3s^1$	Ar $4s^1$	Kr $5s^1$	Xe $6s^1$
Atomic radius (b), A		1·23	1·57	2·03	2·16	2·35
Ionic radius, M^+, A		0·60	0.95	1·33	1·48	1·69
Ionisation energy, eV	I.	5.40	I. 5.14	I. 4.34	I. 4.18	I. 3.90
	II.	76.00	II. 47·40	II. 32·00	II. 28·00	II. 25·00
Electronegativity (c)		1·0	0·9	0·8	0·8	0·7
Density, g cc^{-1}		0·53	0·97	0·86	1·53	1·90
Melting point, °C		179	98	64	39	28·5
Boiling point, °C		1337	880	758	700	670
Standard electrode reduction potential (d), $E°$, V		−3·04	−2·71	−2·92	−2·99	−3·02
Charge to radius ratio		1·67	1·05	0·75	0·68	0·59
$\Delta H^{(e)}_{sub}$ (at 25°C) kcal g^{-1} at^{-1}		36·4	25·9	21·5	20·5	18·8
$\Delta H^{(f)}_{hyd}$ kcal mol^{-1}		−121	−97	−76	−70	−62
$D(M_2)^{(g)}$ kcal mol^{-1}		25	17	12	11	10·4
$\Delta H^{(h)}_{atom}$ at 25°C; 1 atm; kcal mol^{-1}		38	26	21	19·5	18·7

(a) All these have BCC structure; (b) The values are for metallic coordination number=8; (c) Pauling scale; (d) Standard values of $E°$ at 25°C; (e) Enthalpy of sublimation of metal from solid to gaseous state; (f) Heat evolved in the reaction, $M^+ + aq \rightarrow [M(aq)]^+$; (g) Dissociation energy $M_2(gas) + \Delta H \rightarrow 2M(g)$; (h) ΔHatom is the energy required for the process $M(solid) \rightarrow M(atom)$.

16.1.2 Chemical Properties of Alkali Metals
Group IA elements are charaterised by the presence of a single *s*-electron in their outermost shell. This makes these elements univalent in their chemical properties. The first ionisation energies being rather low, these metals readily attain the $+1$ state but formation of the $+2$ state is difficult since the second ionisation energies are quite high.

The low values of the first ionisation energy are reflected in the bond dissociation energies of the gaseous diatomic molecules of alkali metals (Table 16.1). The dissociation energies vary from 25 to 10 kcal mol^{-1}. The low values indicate that alkali metals have little attraction to share an extra electron.

Alkali metals are strong reducing agents, as indicated by the relatively large negative values of their reduction potentials (Table 16.1), with lithium having the highest value. Since all those elements with positive values of oxidation potentials are better reducing agents than hydrogen, alkali metals reduce H^+ in aqueous solution. Thus, these metals react with compounds having acidic hydrogen atoms like water, C_2H_2 and $HX(X=$halogen):

$$2Li + 2H_2O \rightarrow 2\ LiOH + H_2$$
$$2Li + 2HX \rightarrow 2\ LiX + H_2$$
$$2Li + 2HC \equiv CH \rightarrow 2Li—C \equiv CH + H_2$$
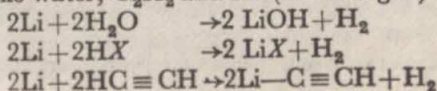
These reactions occur so vigorously that the liberated hydrogen ignites. Thus even the storage of these metals must be in the absence of moisture, under kerosene.

Example 16.1 Explain the fact that amongst alkali metals, lithium has the highest ionisation potential as well as the highest positive oxidation potential.

Ignoring entropy effects, the oxidation potential of an element is the algebraic sum of the following enthalpies.

$$M(s) \rightarrow M(g) \qquad \Delta H_1 \quad \text{(SUBLIMATION ENERGY)}$$
$$M(g) \rightarrow M^+(g) + e \quad \Delta H_2 \quad \text{(IONISATION ENERGY)}$$
$$M^+(g) + aq \rightarrow M^+(aq) \qquad \Delta H_3 \quad \text{(HYDRATION ENERGY)}$$
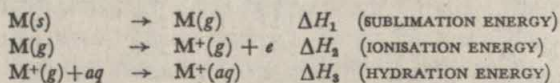
In the first group of elements, the sublimation energy does not vary greatly from lithium to cesium (see Table 16.1), but the ionisation and hydration energies decrease. However, the decrease in hydration energy is so large that the algebraic sum of all the three energies becomes maximum for lithium. This is responsible for the higher value of oxidation potential of lithium with respect to other alkali metals.

Alkali metals dissolve in liquid ammonia to form blue solutions which upon standing gradually liberate hydrogen. We see that this reaction is similar to the reaction between alkali metals and water.

$$2\,Na + 2\,HNH_2 \rightarrow 2\,NaNH_2 + H_2$$
$$2\,Na + 2\,HOH \rightarrow 2\,NaOH + H_2$$
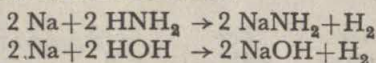
The blue colour of metal-ammonia solutions is supposed to arise from the solvated electron.

The *heats of hydration* of alkali metal ions (Table 16.1) are smaller than those of other metallic ions. This is because alkali metal ions as a group have relatively smaller values of the ratio of the charge to radius. If a metal ion has higher value of this ratio, it can polarise water molecule more, forming a stronger metal to oxygen bond giving relatively higher hydration energy. Within the group, lithium has the highest charge to radius ratio and has therefore the highest hydration energy in the group.

Example 16.2 The ionisation of sodium in liquid ammonia may be written in the following way:

$$Na(s) + NH_3\,(l) \rightarrow [Na(NH_3)_p]^+ + [e(NH_3)_q]^-$$
$$[e(NH_3)_q]^- \rightarrow H\cdot + [(NH_2)\,(NH_3)_{q-1}]^-$$
$$2H\cdot \rightarrow H_2$$

Total: $2Na + 2NH_3 \rightarrow 2Na^+ + 2NH_2^- + H_2$
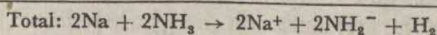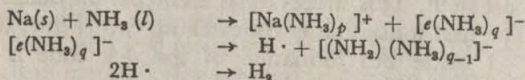
(a) Write analogous equations for the reaction of sodium with water.

$$Na(s) + H_2O \rightarrow [Na(H_2O)_p]^+ + [e(H_2O)_q]^-$$
$$[e(H_2O)q]^- \rightarrow H\cdot + [(OH)\,(H_2O)_{q-1}]^-$$
$$2H\cdot \rightarrow H_2$$

Total: $2Na + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_2$
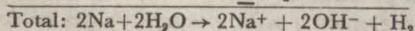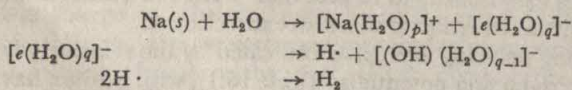
Example 16.3 The heats of formation of normal oxides become less exothermic in the order $Li_2O > Na_2O > K_2O$. Suggest the sequence you would expect in the heats of formation of group IA sulphides.

Generally, heats of formation of analogous group IA compounds vary in the order $K > Na > Li$.

With small anions like O^{2-} or F^-, however, this normal order is frequently reversed.

The following sequence is found in the heats of formation of sulphides: $K_2S > Na_2S > Li_2S$

16.1.3 Oxides and Hydroxides

Among the alkali metals, only lithium reacts directly with oxygen to give the simple monoxide Li_2O. The direct reaction between sodium and oxygen gives sodium peroxide Na_2O_2. The other alkali metals react with oxygen to form superoxides of the general formula MO_2, which contain the superoxide ion, O^-_2. These oxides are ionic compounds. They are all strong bases and dissolve readily in water with the evolution of a large amount of heat

$$M_2O(s) + H_2O \rightarrow 2M^+(aq) + 2OH^-(aq) + \Delta H$$
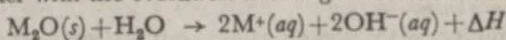
The bases formed by dissolving oxides are called alkalies. The alkalies except lithium hydroxide are all highly soluble in water and are thermally stable illustrating the strong electropositive nature of the metals. The exceptional character of lithium hydroxide can be attributed to the relatively small size of the lithium ions (see discussion of this aspect later in this section).

16.1.4 Alkali Metal Halides

Alkali metals react with halogens directly and vigorously to form metal halides of the general formula MX (where $X=$F, Cl, Br, or I.) These halides are cryst-alline ionic substances with high melting and boiling points. Fused halides like NaCl are good conductors of electricity. All the halides excepting lithium fluoride are freely soluble in water. The insolubility of lithium fluoride is attributed to the high lattice energy of the compound resulting from the combination of the very small lithium cation with fluoride anion. Table 16.2 gives the solubilities of LiF, NaCl, NaI and RbCl along with their respective lattice and hydration energies. The data in the table show that the solubilities of the salts are related to more fundamental properties like lattice and hydration energies.

Table 16.2 Lattice and Hydration Energies and Solubilities of Some Alkali Metal Halides

Halides	$\Delta H_{lattice}$ kcal mol^{-1}	ΔH_{hydr} kcal mol^{-1}	$\Delta H_{lattice} + \Delta H_{hydr}$ kcal mol^{-1}	Solubilities mol litre^{-1}
LiF	247	-240	$+7$	0·11
NaCl	186	-185	$+1$	6·1
NaI	166	-168	-2	11·0
RbCl	162	-159	$+3$	7·5

Example 16.4 The free energy of formation of NaCl, $\Delta G_f°$, is -92 kcal mol^{-1}. What conclusions can you draw regarding its stability from this information?

The equilibrium constant, K for the reaction $Na(s) + \frac{1}{2}Cl_2(g) \rightleftharpoons NaCl(s)$ at 25°C is given by

$$K = \frac{1}{(p_{Cl_2})^{\frac{1}{2}}} = e^{-\Delta G_f°/RT} \approx 10^{67}$$

A large value $K(10^{67})$ means that the partial pressure of chlorine in equilibrium with $Na(s)$ and $NaCl(s)$ is very low (of the order of 10^{-134} atm) and therefore sodium chloride is highly stable. Other alkali halides also show similar behaviour.

16.1.5 Hydrides

Crystalline, ionic hydrides of the general formula MH are formed by the direct reaction of hydrogen with alkali metals. The hydrogen is present as H^- (i.e. hydride anion) in these compounds. Electrolysis of alkali hydrides produces hydrogen gas at the anode, while the metal deposits at the cathode. This is an indication of the ease with which alkali metals lose their valence electron to form cations. In addition to these simple hydrides, alkali metals such as lithium are known to form complex hydrides of the type $LiBH_4$ and $LiAlH_4$, which are excellent reducing agents. $LiBH_4$ is known to have the ionic strcture $Li^+ BH_4^-$.

16.1.6 Other Reactions

Alkali metals combine with various non-metals to form ionic compounds. Some of the reactions are given in Table 16.3. For the sake of completeness, the reactions already described are also included in the table.

Alkali metals, as well as many of their compounds, impart characteristic colours to a gas flame: lithium imparts crimson colour; sodium, yellow; potassium, violet; rubidium, red; and cesium, blue. These characteristic colours of the flame are employed in the detection of these elements (see Chapter 3 for a discussion of atomic spectra).

Table 16.3 Reactions of Group IA Metals

Reaction	Reaction
$2M + H_2 \rightarrow 2MH$ (hydride)	$4Li + O_2 \rightarrow 2Li_2O$ (oxide)
$2M + 2C \rightarrow 2MC$ (carbide)	$2Na + O_2 \rightarrow Na_2O_2$ (peroxide)
$6Li + N_2 \rightarrow 2Li_3N$	$M + O_2 \rightarrow MO_2$ (superoxide)
$12M + P_4 \rightarrow 4M_3P$	$2M + X_2 \rightarrow 2MX$ (X=halogen)
$2M + S \rightarrow M_2S$	$2M + H_2SO_4 \rightarrow M_2SO_4 + H_2$
$2M + Se \rightarrow M_2Se$	$2M + 2NH_3 \rightarrow 2MNH_2 + H_2$

16.1.7 Anomalous Behaviour of Lithium
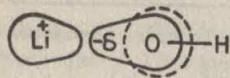
Fig. 16.1 The distortion or polarisation of hydroxide ion by Li^+ ion in LiOH. Due to polarisation, the OH bond becomes weaker.

While many properties of lithium are similar to those of the other members of the group, there are several dissimilarities as well. These anomalies mainly result from the small size of the lithium ion or atom. As stated earlier, the polarising power of Li^+ (due to its *large charge to radius ratio*) is larger than that of any other alkali metal ion and this leads to a greater preference for covalent bond formation (Fig. 16.1). Thus, the hydroxide, carbonate and nitrate of lithium decompose on heating to give the oxides of lithium. Similar compounds of other alkali metals do not decompose so readily.*

*The reason for this is as follows: The nucleus of the cation attracts the electrons of the anion, so that the electron density about the anion is greater in the direction of the cation. The anion also has similar, but weaker effect on the cation. Small size and high charge (large charge to radius ratio) favour the polarising ability of cation. Thus, lithium ion being much smaller than sodium or potassium ion has a large polarising ability. With the result, the covalent character of the Li—O bonds in these compounds is higher compared to that of Na—O or K—O bond. This makes the Li—O bond stronger than other alkali metal—oxygen bonds.

16.1.8 Occurrence, Preparation and Uses of Alkali Metals

Alkali metals, being very reactive, do not occur in free state in nature. They are always found in the form of their compounds. Compounds of sodium and potassium occur abundantly in nature, whereas those of rubidium and cesium occur only sparingly. All the alkali metals occur as compounds of mixed oxides or halides. For example, potassium occurs abundantly as the mineral *feldspar*, $K_2O \cdot Al_2O_3 \cdot 3SiO_2$. Lithium occurs in nature as lithium ions in several types of rocks of complex composition. Rubidium and cesium occur to a small extent in similar mixed oxide minerals. The most abundant compound of sodium in nature is sodium chloride (common salt). Potassium chloride occurs to a limited extent in nature. Francium occurs naturally in only trace amounts and all its isotopes are radioactive. Trace amounts of francium have been prepared by nuclear reactions.

To prepare alkali elements, it is necessary to reduce the alkali metal ion. This can be done chemically or electrolytically. In practice, alkali metals are generally prepared by the electrolysis of the molten alkali metal chlorides. For example, metallic sodium is prepared industrially by the electrolysis of a fused mixture of sodium and calcium chlorides at about 600°C. Calcium chloride is added to lower the melting point of sodium chloride. Sodium metal is formed at the cathode, and chlorine at the anode.

All the alkali metals are excellent conductors of heat and electricity. Sodium-filled iron pipes, for example, are employed as conductors of electricity. Sodium metal is used in the manufacture of several compounds, such as sodium hydride, NaH; sodium peroxide, Na_2O_2; sodium cyanide, $NaCN$; and sodamide, $NaNH_2$. Sodium is used in the production of tetraethyl and tetramethyl lead, the antiknock additives for gasoline. Liquid sodium, an excellent heat conductor, is employed as a coolant in some nuclear reactors. The ease with which cesium loses electrons is made use of in photoelectric cells. This property is also the basis for the exploratory development of a cesium-ion engine for use in space exploration. A very important application of sodium metal is in the manufacture of sodium-vapour lamps, which are now widely used in street lighting. Sodium is also used in the manufacture of many dyes. Lithium metal is used in the manufacture of special alloys and in the synthesis of certain organic compounds. An important use of potassium metal is in the synthesis of potassium superoxide; this is used as a source of oxygen at high altitudes.

16.2 GROUP IIA ELEMENTS : ALKALINE EARTH METALS

The six elements beryllium, magnesium, calcium, strontium, barium and radium, occupying group IIA of the periodic table, are known as the alkaline earth metals. They immediately follow alkali metals in the periodic system.

16.2.1 General Characteristics

Ignoring the filled core orbitals, the electronic configuration of the alkaline earth metals may be written ns^2 (Table 16.4).

Metals of this group are considerably harder than the alkali metals, beryllium being hard enough to scratch glass. The hardness decreases with the increase in atomic mass. The melting and boiling points are higher than those of the alkali metals (Table 16.4). These differences in properties can be explained in terms of stronger metallic bonds in the alkaline earth metals (two valence electrons).

Table 16.4 Physical Properties of the Group IIA Elements

Property	Element				
	Beryllium	Magnesium	Calcium	Strontium	Barium
Atomic mass	9·0	24·3	40·0	87·6	137·4
Atomic number	4	12	20	38	56
Isotopes	9	24, 25, 26	40, 42, 43, 44, 46, 48	84, 86, 87, 88	130, 132, 134, 138
Electronic structure	$1s^2 2s^2$	Ne $2s^2$	Ar $3s^2$	Kr $4s^2$	Xe $5s^2$
Atomic radius, [a] A	1·06(12)	1·40(12)	1·74(12)	1·91(12)	1·98(8)
Ionic radius, M^{2+}, A	0·30	0·65	0·99	1·10	1·29
Ionisation energy, eV	I. 9·32 II.18·21	I. 7·64 II.15·03	I. 6·11 II.11·67	I. 5·69 II.11·00	I. 5·21 II.10·00
Electronegativity	1·5	1·2	1·0	1·0	0·9
Density, g cc^{-1}	1·86	1·74	1·55	2·54	3·59
Melting point, °C	1280	650	842	774	850
Boiling point °C	2970	1100	1240	1366	1527
Standard electrode reduction potential, $E°$, V	−1·69	−2·34	−2·87	−2·89	−2·90
ΔH_{hyd} M^{2+}, kcal mol^{-1}	−570	−460	−395	−355	−305
ΔH_{atom} (at 25°C, 1 atm), kcal mol^{-1}	78·2	35·1	42·3	39·0	42·0

For explanation of the symbols in the table refer to Table 16.1. [a] The metallic coordination number is given in brackets.

16.2.2 Trends in Chemical Properties

Beryllium differs from the rest of the group and behaves more like aluminium, the second member of group IIIA. Because of its small size and high charge density, beryllium is predominantly covalent in its compounds. With the exception of beryllium, the other members of this group have a relatively greater tendency to give up the two valence electrons to electronegative elements like oxygen, sulphur and halogens, to form ionic compounds:

$$Mg + S \rightarrow Mg^{2+} S^{2-} (s)$$
$$Ca + \tfrac{1}{2}O_2 \rightarrow Ca^{2+} O^{2-} (s)$$
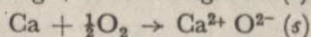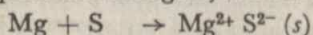
Alkaline earth elements form only dipositive ions. The removal of a third electron from these metals requires very high energy (1840 kcal mol^{-1} in the case of magnesium), as the third electron has to come from a completed noble gas configuration. The chemistry of these elements, is, therefore, the chemistry of dipositive ions.

16.2.3 Reactivity of the Alkaline Earth Metals

All the metals of this group burn in oxygen forming oxides. Beryllium, magnesium and calcium form monoxides, but strontium and barium form peroxides. The reactivity of these elements with oxygen increases as we move down the group from beryllium to barium.

The increasing reactivity of alkaline earth metals is also reflected in their reaction with water to produce the hydroxides and hydrogen. Beryllium, the first member of the group, is practically unaffected by water at ordinary

temperatures, but reacts at higher temperatures. However, barium reacts vigorously with cold water.

$$M(s) + 2H_2O \ (l) \rightarrow M^{2+} \ (aq) + 2OH^- \ (aq) + H_2 \ (g)$$
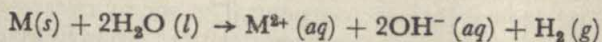
16.2.4 Hydration of the Alkaline Earth Metal Ions

The sizes of alkaline earth atoms and ions, and their heats of hydration are given in Table 16.4. The heat of hydration decreases with the increase in ionic size. To get some idea of the influence of the charge of the cation on the heat of hydration, let us compare an alkali metal ion and an alkaline earth metal ion of approximately the same size (see Tables 16.1 and 16.4): Na^+ (0·95A) and Ca^{2+} (0·99 A). Although these two ions are almost of the same size, the heat of hydration of the dipositive Ca^{2+} (395 kcal) is approximately four times that of the monopositive Na^+ (95 kcal). The same comparison holds good for Ba^{2+} and K^+. Thus, the alkaline earth metal ions, because of their small size and greater positive charge exert much stronger electrostatic attraction on the oxygens of water.

Example 16.5 Show that gaseous Ca^+ is stable with respect to gaseous calcium and Ca^{2+}, but $Ca^+(aq)$ is unstable with respect to Ca^{2+} (aq) and calcium metal.

Consider the following energetics:

$$
\begin{array}{lll}
Ca(g) = Ca^+ \ (g) + e & \Delta H = & 140 \ \text{kcal} \\
Ca^{2+} \ (g) + e = Ca^+ \ (g) & \Delta H = & -274 \ \text{kcal} \\
\hline
Ca^{2+} \ (g) + Ca(g) = 2Ca^+ \ (g) & \Delta H = & -134 \ \text{kcal}
\end{array}
$$
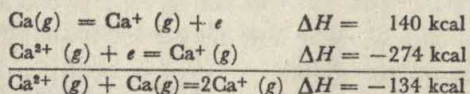
This shows that Ca^+ (g) is more stable than Ca^{2+} (g) and $Ca(g)$.

Again,

$$
\begin{array}{llll}
2 \ Ca^+ \ (g) + (aq) & \rightarrow & 2 \ Ca^+ \ (aq) & \Delta H = -152 \ \text{kcal} \\
Ca(s) & \rightarrow & Ca(g) & \Delta H = \ \ \ 42 \ \text{kcal} \\
Ca^{2+} \ (aq) & \rightarrow & Ca^{2+}(g) + aq & \Delta H = \ \ 395 \ \text{kcal} \\
Ca(g) + Ca^{2+} \ (g) & \rightarrow & 2 \ Ca^+ \ (g) & \Delta H = -134 \ \text{kcal} \\
\hline
Ca(s) + Ca^{+2} \ (aq) & \rightarrow & 2 \ Ca^+ \ (aq) & \Delta H = +151 \ \text{kcal}
\end{array}
$$
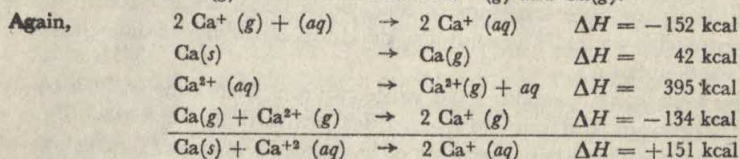
Thus Ca^+ (aq) is less stable with respect to $Ca(g)$ and Ca^{2+} (aq).

16.2.5 Alkaline Earth Metals as Reducing Agents

Since alkaline earth metals (except Be) tend to lose their valence electrons easily, they act as strong reducing agents. The oxidation potentials of these elements can be considered to be sum of energies of three reactions:

$$
\begin{array}{lll}
M(s) & \rightarrow M^{2+}(g) + 2e^- & \Delta H_1 = \text{IONISATION POTENTIAL} + \\
& & \qquad \quad \text{SUBLIMATION ENERGY} \\
M^{2+}(g) + aq & \rightarrow M^{2+} \ (aq) & \Delta H_2 = \text{HYDRATION ENERGY} \\
\hline
M(s) + (aq) & \rightarrow M^{2+} \ (aq) + 2e^- & \Delta H = \Delta H_1 + \Delta H_2
\end{array}
$$
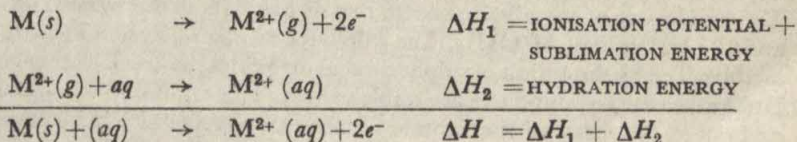
The oxidation potentials of alkaline earths are relatively high (Table 16.4). If we compare the oxidation potentials of the alkali and the alkaline earth metals, we notice that there is a distinct difference between the lighter elements of the two groups. For example, the oxidation potential of beryllium is $+1·85V$ compared to $+3·05V$ of lithium. However, as we go down the group, there is a similarity between the alkali metals and the corresponding alkaline earths. Since the alkaline earth metals have higher ionisation energies compared

35

to alkali metals, we would have expected them to be less effective reducing agents. However, alkaline earths are as good reducing agents as alkali metals because of their higher hydration energy. The energy released during the hydration of ions is more than sufficient to pull the two electrons from the atom.

16.2.6 Oxides and Hydroxides

Oxides of alkaline earth metals are extremely stable solids and their free energies of formation are highly negative and are in the range -126 to -144 kcal mol^{-1} at 25°C. These are formed either by burning the metal or by the thermal decomposition of their respective carbonates. Beryllium oxide is distinguished from other oxides by a larger degree of covalency. It is polymeric and is, therefore harder; beryllium oxide is *amphoteric* and reacts slowly with strong acids to form hydrated ions $[Be(H_2O)_4]^{2+}$. It also reacts with strong bases and enters into solution as the ion $[Be(OH)_4]^{2-}$.

Example 16.6 Why is beryllium oxide amphoteric?

Beryllium ion is comparatively small and hence has a relatively large charge to radius ratio. Consequently, it polarises the surrounding molecules by drawing electrons from them. Thus, in $[Be(H_2O)_4]^{2+}$, beryllium ion will withdraw electronic charge from oxygen of water towards itself and will facilitate the removal of protons and formation of $[Be(OH)_4]^{2-}$. In this way $[Be(H_2O)_4]^{2+}$ is an acid and $[Be(OH)_4]^{2-}$ a base.

The oxides react with water to form the corresponding hydroxides with the evolution of a large amount of heat.

$$MO(s) + H_2O(l) \rightarrow M(OH)_2(s) + \text{HEAT}$$
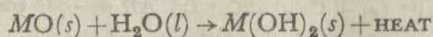
Beryllium oxide shows little tendency to react with water while barium oxide reacts vigorously with water. The solubility products of the hydroxides decrease as we go down the group.

Magnesium hydroxide is weakly basic while calcium hydroxide is a relatively strong base. Strontium and barium hydroxides are both strong bases. This is understandable since the basic character of hydroxides increases as the size of metal ion increases. These hydroxides being strong bases, react with acids and also dissolve in water to produce $M^{2+}(aq)$ and OH^-. The increasing solubility of the hydroxides as we go down the group from Be^{2+} to Ba^{2+} results principally from the decrease in lattice energy.

16.2.7 Carbonates and Sulphates

The carbonates of the alkaline earth metals are salts of the weak acid, H_2CO_3 and the hydroxides, $M(OH)_2$. The sulphates of alkaline earth metals, MSO_4, are obtained by the action of sulphuric acid on oxides, hydroxides or carbonates. Unlike carbonates, sulphates are stable to heat. The solubilities of sulphates and carbonates decrease as the atomic number of the metal ion increases. (For example, the solubility product of $CaCO_3$ is $4·7 \times 10^{-9}$ while that of $CaSO_4$ is $2·4 \times 10^{-5}$.) This behaviour is opposite to that observed for the hydroxides.

Solubility depends on two factors, (i) lattice energy and (ii) hydration energy. For the alkaline earth sulphates (or carbonates), the lattice energies are comparable, apparently because the sulphate ion (or carbonate ion) is so large (about 3 A radius) that changing the size of the much smaller cation makes little difference. The difference in solubility must, therefore, be due to the difference in hydration energy. As we proceed in the sequence from Be^{2+} to Ba^{2+}, the hydration energy of the positive ion becomes smaller because of the increase

in ionic size. This tends to make the sulphates and carbonates of the heavier metal ions less soluble than those of the lighter ones.

Beryllium carbonate is unstable. The stability of other carbonates (or the decomposition temperature) increases with the size of the metal ion. Barium carbonate must be heated to a very high temperature to bring about the decomposition into barium oxide and carbon dioxide. Decomposition of carbonates is endothermic. The differences in stabilities of carbonates can be understood in terms of the attraction of the metal ions for the oxide ion (see section 16.1.7).

16.2.8 Alkaline Earth Halides

Alkaline earth metals react with halogens directly and vigorously to form metal halides of the general formula, MX_2, where X is the halogen. Beryllium chloride has a lower melting point as well as electrical conductivity in the fused state than the other alkaline earth chlorides. Further, beryllium chloride is soluble in organic solvents suggesting the non-polar character of the compound. The small and highly charged beryllium ion polarises neighbouring negative ions and the

Fig. 16.2 Structure of beryllium chloride
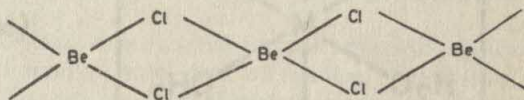
degree of polarisation is so large that we can think of beryllium chloride as a covalently bonded molecules. In the solid state, Be forms tetrahedral covalent bonds with chlorine resulting in Be—Cl—Be bridged structure (Fig. 16.2).

Among the chlorides, there is a regular increase in the melting point as the size of the metal ion increases. Similarly, the conductivity of the metal chlorides increases from beryllium to barium. This increase can be attributed to the increasing ionic character of chlorides. Thus barium chloride is a stable high melting solid and a conductor of electricity in the molten state.

Ionic alkaline earth chlorides dissolve in water to produce neutral solutions of hydrated divalent metal ions and hydrated chlorine ions. When their solutions are evaporated, the following colourless hydrated salts are crystallised: $MgCl_2 \cdot 6H_2O$; $CaCl_2 \cdot 6H_2O$; $SrCl_2 \cdot 6H_2O$; and $BaCl_2 \cdot 2H_2O$. When covalent beryllium comes into contact with water, it hydrolyses readily to form an acidic solution, according to the following equation:

$$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$$
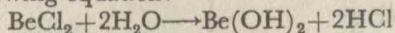
Chlorides of calcium, strontium and barium when introduced into the Bunsen flame impart characteristic colours to the flame. For example, calcium imparts brick red colour; strontium, crimson; and barium, apple green. The colours of the flames are used in the detection of these metals.

The bromides and iodides of alkaline earths are similar to the chlorides. The fluorides are relatively insoluble because of the large values of lattice energies.

16.2.9 Complex Compounds

The higher charge and smaller size of the alkaline earth metal ions, as compared to the alkali metal ions, result in an increased tendency to form *complex* compounds. This effect is of particular importance in the chemistry of beryllium where the small size of the ion favours the formation of stable coordination complexes. Complexes of magnesium are also formed, but less readily than in the case of beryllium; with calcium, strontium and barium, the increased cation size still further diminishes the tendency for complex formation.

Beryllium invariably exhibits the coordination number of four in its complexes. This may be accounted for by the availability of sp^3 hybrid orbitals in the valence shell of Be^{2+}. Since the four bonds formed by beryllium in its complexes involve the use of sp^3 hybrid orbitals the arrangement of these bonds around beryllium will be tetrahedral as in the case of hydrated beryllium ion $[Be(H_2O)_4]^{2+}$.

The absence of d orbitals in the valence shell makes it difficult for beryllium to achieve a coordination number greater than four. Magnesium and calcium on the other hand attain a coordination number of six in their complexes. The six bonding orbitals used by magnesium and calcium in these complexes are sp^3d^2 hybrid orbitals. This results in an octahedral arrangement of the six bonds about the magnesium and calcium ions, as illustrated by the hydrated magnesium and calcium ions, $[Mg(H_2O)_6]^{2+}$, $[Ca(H_2O)_6]^{2+}$, and $[Mg(NH_3)_6]^{2+}$.

$$(M = Mg^{2+} \text{ or } Ca^{2+})$$
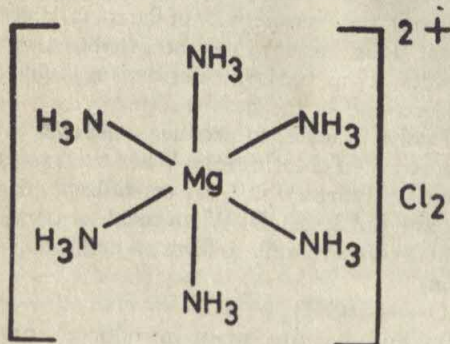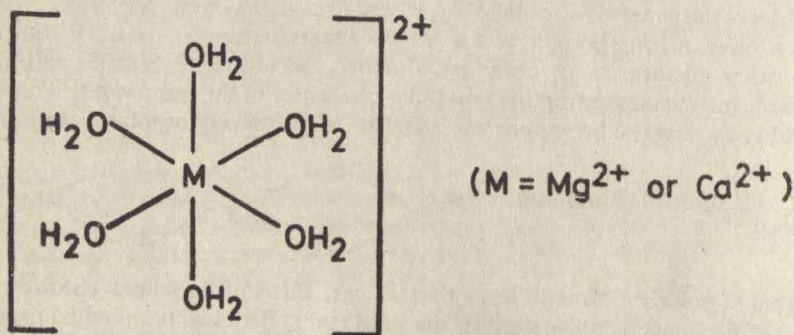
16.2.10 Occurrence, Preparation and Uses of Alkaline Earth Metals

Like the alkali metals, alkaline earth metals are never found in the free form in nature because of their high reactivity. They occur in combined forms as silicates, carbonates, sulphates and phosphates. The most common source of beryllium is the mineral *beryl*, $Be_3Al_2(SiO_3)_6$. Magnesium is the sixth most abundant metal in the earth's crust. It occurs in a great many varieties of siliceous minerals such as *talc*, $H_2Mg_3(SiO_3)_4$ and *asbestos*, $CaMg_3(SiO_3)_4$. Magnesium is found in brine wells and salt deposits in the form of $MgCl_2 \cdot KCl$ (*carnallite* and *dolomite* consisting mainly of the double salt $MgCO_3 \cdot CaCO_3$). *Magnesite*, $MgCO_3$, is less common but is a very valuable magnesium ore. There is an almost unlimited supply of magnesium in the sea, which is the main commercial source of magnesium.

Calcium, the third most abundant of all metals, occurs as a carbonate, $CaCO_3$, in *marble*, *limestone* and *chalk*. Other important calcium minerals include *dolomite*, *anhydrite* ($CaSO_4$), *gypsum* ($CaSO_4.2H_2O$) and *fluorspar* (CaF_2). Barium and strontium are found most frequently as the sulphates, $BaSO_4$ and $SrSO_4$. Radium is present in extremely small amounts in uranium minerals.

All the alkaline earth metals are prepared by the electrolysis of their fused anhydrous halides. Alkali metal halides are added to lower the melting point and to improve the conductivity of the electrolytic mixture.

The metals are also obtained by reduction of their oxides with aluminium metal at high temperature in a vacuum.

$$3BaO + 2Al \rightarrow 3Ba + Al_2O_3$$
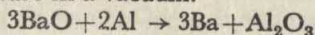
Under these conditions, barium is volatile and escapes from the reaction mixture.

Beryllium being a light metal is used extensively in the manufacture of light alloys. Copper-beryllium alloys are used to make high-strength springs. Beryllium oxide is used to make refractory crucibles designed for high temperature reactions.

As a structural material, however, only magnesium has important applications. It forms alloys with aluminum, zinc, and manganese, yielding light weight and strong materials that are used in aircraft construction. Its high oxidation potential makes it a useful reducing agent in the metallurgy of beryllium, titanium and zirconium and for cathodic protection against the corrosion of iron and steel.

Magnesium powder and magnesium ribbon find many uses in flash powders and flash bulbs, incendiary bombs, and signals. A suspension of magnesium hydroxide, $Mg(OH)_2$, in water, commonly known as *milk of magnesia*, is used medicinally as an anti-acid. Magnesium carbonate also serves as an ingredient in tooth pastes. Calcium and barium combine with ease with oxygen and nitrogen at elevated temperatures, and therefore are used to remove traces of air from vacuum tubes. Calcium metal is used to remove oxygen from metal oxides in the manufacture of alloys and special steels. Radium compounds are used mainly in the treatment of cancer.

16.3 GROUP IIIA ELEMENTS: BORON FAMILY

The elements boron and aluminium together with gallium, indium, and thallium constitute group IIIA of the periodic table.

16.3.1 General Characteristics

The electronic confiugrations of group IIIA elements are core ns^2np^1. Their properties are affected to some extent by the size of the atoms and ions. Unlike groups IA and IIA where there is close resemblance between the family members, the elements of this group show a range of properties with some dissimilarities within the group. For example, in group IIIA we have the semimetallic element, boron, and also the metallic element like thallium. Such contrasts are also seen in the elements of groups IVA, VA and VIA. The important physical properties of the elements boron and aluminum are given in Table 16.5.

Except for boron, the other elements of group IIIA are classified as metals. Boron is a hard, brittle substance with a dull metallic lustre. It is a poor conductor of electricity. Aluminium on the other hand has the properties of a

metal and is a good conductor of heat and electricity. The melting and boiling points of boron are higher than those of aluminium showing that the atoms of boron are held in the crystal lattice and in the liquid by stronger bonds.

In spite of the large nuclear charge and small size, the first ionisation energies of boron and aluminium are lower than those of beryllium and magnesium since the p electrons are less penetrating and more shielded than the s electrons. The total energy required to produce M^{3+} ions (sum of first three ionisation energies) is very high and these elements therefore tend to form covalent bonds rather than trivalent ions. This is especially true in the case of boron whose compounds resemble those of non-metals like silicon.

Table 16.5   Physical Properties of Boron and Aluminium[1]

Property	Element	
	Boron	*Aluminium*
Atomic mass	10·88	26·98
Atomic number	5	13
Isotopes	10, 11	27
Electronic structure	$1s^2 2s^2 2p^1$	$1s^2 2s^2 2p^6 3s^2 3p^1$
Atomic radius, A	0·80	1·25
Ionic radius, M^{3+}, A	0·20	0·50
Ionisation energy, eV	I. 8·33	I. 5·96
	II. 25·00	II. 18·75
	III. 37·75	III. 28·40
Standard electrode reduction potential, $E°$, V	−0·87	−1·67
Electronegativity	2·0	1·50
Density, g cc⁻¹	2·3	2·7
Melting point, °C	2000	660
Boiling point, °C	3700	2660

[1]For explanations of the symbols see Table 16.1.

The metallic lattices of the other elements are much more readily ruptured, and melting points are significantly lower. Boiling points are generally high and decrease in general with increasing atomic mass. Except for boron, the elements of this family exist as liquid over considerable temperature range. This property is most pronounced with gallium. It is a liquid at ordinary pressure over a range of 2000°C and has been employed for high temperature thermometry in a quartz envelope. It has a strong tendency to superfusion and will remain liquid at room temperature for a considerable period.

With the increase in atomic mass the ionic character of bonds formed by the group IIIA elements increases, and some of the heavier metal ions do exist in the +3 oxidation state in aqueous solution. The stability of such compounds with the +3 oxidation state is, however, lower than those with the +1 oxidation state in the case of heavier members of this group. Thus, thallium in +1 oxidation state is more stable than in +3 state. This is because, the s electrons in the ns sub-shell do not prefer to form bonds. This inertness is found only, (i) when the s electrons are in the fifth or higher principal quantum number and (ii) when their loss does not afford a species with a noble gas configuration. This

property of stabilising the lower oxidation state keeping the paired electron in the *ns* orbital is referred to as the *inert pair effect*. This effect is also observed in the elements of groups IIB, IVA and VA where the heavier elements exhibit 0, $+2$ and $+3$ oxidation states respectively.

Aluminium forms compounds in which it exhibits oxidation states of $+1$ and $+2$ although these compounds are unstable at room temperature; they are stable only at high temperatures in the gaseous state. Boron in its trivalent compounds exhibits sp^2 hybridisation with one vacant p orbital. The vacant p orbital has a great tendency to accept a pair of electrons from some other donor atom or a base (electron donor) like ammonia or ether. Thus, many of the boron compounds are Lewis acids; after accepting a pair of electrons, boron atom acquires sp^3 hybridisation as in the 1 : 1 adducts of BF_3 with amines, ethers sulphides and NH_3 (see Chapter 4). The triply charged ions of aluminium and boron, because of the larger nuclear charge, have smaller radii than do the singly charged alkali metal or the doubly charged alkaline earth metal ions.

Aluminium is not a very active metal compared to alkali and alkaline earth metals. Even then it is an excellent reducing agent, as shown by the oxidation potential (Table 16.5).

$$Al(s) \rightarrow Al^{3+}(aq) + 3e \qquad (E^\circ = 1.67 \text{ V})$$
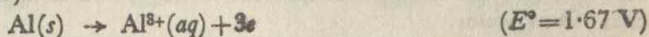
In view of the high ionisation energies of aluminium (first 138 kcal; second 434 kcal; third 656 kcal mol^{-1}), its high oxidation potential is somewhat surprising. It is the hydration energy of the ion which enables the reaction to proceed. It has been estimated that over 1000 kcal of heat are evolved when 1 mole of Al^{3+} is hydrated. The main reasons for this large hydration energy are the high charge to radius ratio.

Example 16.7 The standard oxidation potentials for the following reactions are:

$$Tl \rightleftharpoons Tl^+ + e^- \qquad E^\circ = -0.336 \text{ V}$$
$$Tl^+ \rightleftharpoons Tl^{3+} + 2e^- \qquad E^\circ = 1.25 \text{ V}$$
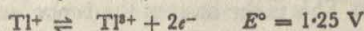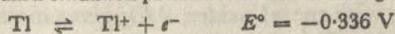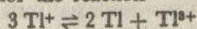
Calculate the equilibrium constant for the reaction
$$3 Tl^+ \rightleftharpoons 2 Tl + Tl^{3+}$$
and predict whether Tl^+ will disproportionate or not in aqueous solution.

The standard half-cell potential for the reaction
$$3 Tl^+ \rightleftharpoons 2 Tl + Tl^{3+}$$
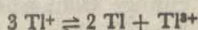
is $1.25 - (-0.336) = 1.586$ V

Now $\qquad \log K = (n/0.059) E^\circ = 2 \times 1.586/0.059 = 54$

Therefore $K = 10^{54}$

This indicates Tl^+ will disproportionate in aqueous solution into Tl and Tl^{3+}.

16.3.2 Oxides

At ordinary temperatures, boron is inert towards oxygen. But in the case of aluminium, there is a rapid reaction on the surface. A thin film of the oxide is formed on the surface of the metal which prevents further oxidation. When amalgamated with mercury, which prevents formation of an adherent film, aluminium is rapidly corroded in moist air and dissolves readily in water with evolution of hydrogen. Gallium and indium are stable in air. Thallium is more reactive and is superficially oxidised in air.

When strongly heated in air, boron and aluminium burn—the former with a green flame and the latter with a brilliant white light to form acidic B_2O_3 and amphoteric Al_2O_3 respectively.

Aluminium oxide is so stable that metallic aluminium (powdered) will reduce a large number of metallic oxides to the metallic state.

$$2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3 \qquad \Delta H = -126 \text{ kcal}$$
$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe \qquad \Delta H = -203 \text{ kcal}$$
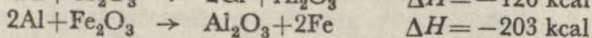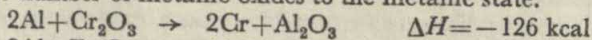
Such reactions proceed with a large evolution of heat and the reduced metal is obtained in the molten state. This reduction of metal oxides by aluminium is known as the *thermite reduction*. This process is useful in welding.

16.3.3 Hydroxides

The hydroxy compounds of boron and aluminium are formed when their oxides react with water. The low ionic radii and the high charges of the ions ($+3$) of the aluminium family account for the fact that the acidic properties of hydroxides become less pronounced with increasing ionic radius. B_2O_3, when hydrated, forms boric acid, $B(OH)_3$ which is a weak acid ($pK = 9$), moderately soluble in water. In its reaction with water, it acts as a Lewis acid accepting OH^- from water.

$$B(OH)_3 + H—OH \rightarrow B(OH)_4^- + H^+$$
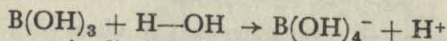
In this reaction boron again displays its tendency to accept a pair of electrons from the Lewis base OH^-. At lower concentrations, monomeric species like $B(OH)_3$, $[B(OH)_4]^-$ are present while at higher concentrations ($>0.03M$), these monomeric species get polymerised with the formation of polymeric species like $[B_3O_3(OH)_4]^-$.

When heated to about $100°C$, orthoboric acid H_3BO_3 loses water to form metaboric acid, HBO_2. At red heat, complete dehydration to the oxide, B_2O_3, takes place. On heating with metal oxides, B_2O_3 gives metaborates which often have characteristic colours. This is the basis of the *borax bead test*. Boric acid is a mild antiseptic.

The hydroxides of aluminium and gallium are amphoteric and react as bases in the presence of hydronium ions, and as acids in the presence of hydroxide ions.

Indium and thallium hydroxides have practically no amphoteric character and act as bases. Thus, this change from acidic to basic behaviour of the hydroxides while going from B to Tl shows a change from non-metallic to metallic behaviour. The same trend is observed in the hydrolysis of the M^{3+} ions. Al^{3+} and Ga^{3+} are partially hydrolysed while In^{3+} and Tl^{3+} are hydrolysed to a negligible degree.

16.3.4 Hydrides

Boron forms a series of volatile compounds with hydrogen called the boranes. The names and properties of several members of the series are listed in Table 16.6. Diborane, B_2H_6, the simplest of these hydrides can be prepared by the reaction of lithium hydride with boron trifluoride.

$$6LiH + 8BF_3 \rightarrow 6LiBF_4 + B_2H_6$$
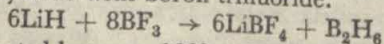
When diborane is heated between $100°$ and $250°C$, it is converted to a mixture of a large number of boranes such as B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}. The formulae of boranes are of two types, B_nH_{n+4} and B_nH_{n+6}, compounds of the first type being more stable.

Most of the boranes are spontaneously inflammable in air and are rapidly hydrolysed by water to boric acid:

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$$
$$B_2H_6 + 6H_2O \rightarrow 2B(OH)_3 + 6H_2$$
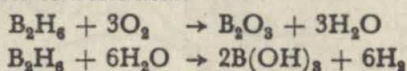
Table 16.6 Properties of Some Boranes

Formula	Name	Reaction with air at 25°C	Melting point °C	Boiling point °C	Reaction with water
B_2H_6	Diborane-6	Spontaneously inflammable	−165·5	−92·5	Instantaneous hydrolysis
B_4H_{10}	Tetraborane-10	Inflammable	−121·6	18	Slow hydrolysis
B_5H_9	Pentaborane-9	Spontaneously inflammable	−46·6	48	Hydrolysis on heating
B_5H_{11}	Pentaborane-11	-do-	−123	63	Rapid hydrolysis
B_6H_{10}	Hexaborane-10	Stable	−62·3	108	Slow hydrolysis
B_6H_{12}	Hexaborane-12	-do-	−83	80–90	Hydrolysis on heating
B_9H_{15}	Enneaborane-15	-do-	2·6	—	—
$B_{10}H_{14}$	Decaborane-14	-do-	99·7	213	Slow hydrolysis

From the point of view of bonding, boranes are a very interesting series of compounds. Let us consider the simplest member of the series, diborane (B_2H_6). The electron configuration of boron predicts that the atom should be trivalent as in BF_3. We would, therefore, expect that the simplest hydride of boron should have the formula BH_3. However, no such compound has been isolated and we get only the dimer, diborane. The geometry of B_2H_6 shows (Fig. 16.3) that the boron atoms and the four terminal hydrogen atoms are in one plane while the remaining two hydrogen atoms are in a plane perpendicular to the first one. Such a structure is inconsistent with the concept of an electron-pair bond since there are eight B—H bonds in B_2H_6 whereas there are only twelve valence electrons. Obviously, there are not enough electrons to form eight electron pair bonds. Similar situation exists for all the other boranes which are, therefore, known as *electron deficient compounds*.
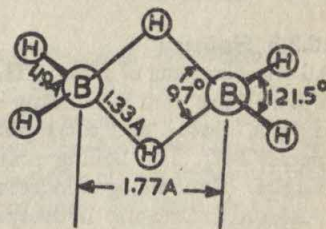
Fig. 16.3 Structure of diborane

Let us see how the bonding theory tackles this problem. Since the four bonds around each boron atom are roughly tetrahedral, one starts with the sp^3 hybrid orbitals on the boron atoms. Four out of these eight hybrids overlap with the 1s orbitals of the hydrogen atom to give four B—H bonds — two on each boron atom. All these B—H bonds are in the same plane while the remaining four sp^3 hybrids are in a plane perpendicular to it. One hybrid from each boron atom can combine with the 1s orbital of one of the bridge hydrogens to form a molecular orbital which is spread over three atoms. Such an orbital is called a *three centre orbital* (Fig. 16.4). Another three centre orbital involves the other set of the hybrid orbitals and the 1s orbital of the second bridge hydrogen. Just as the combination of two atomic orbitals leads to two
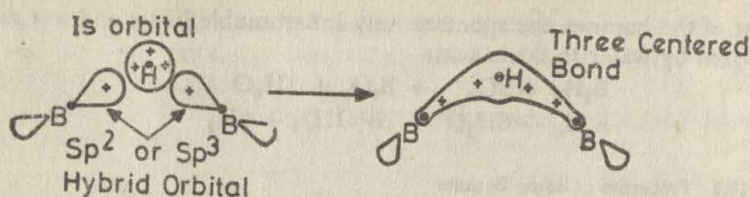
Fig. 16.4 Formation of a three-centre B—H—B bond in boron hydrides

molecular orbitals, combination of three atomic orbitals generates three molecular orbitals—a bonding one which is lower in energy, an antibonding one which is higher in energy, and a non-bonding one which has the same energy as the separated atoms. Thus, for the two B—H—B bridges, we have two bonding, two non-bonding and two antibonding orbitals which have to accommodate four valence electrons. Consequently, the lowest energy bonding orbitals get occupied leaving the non-bonding and the antibonding orbitals vacant. In other words, a pair of electrons acts as a bond between three centres or atoms. Such a bond is known as a *three centre bond* or sometime as *banana bond*. It is possible to extend this idea further where a pair of electrons binds more than three atoms or centres (multi-centre bonds). This type of bonding is encountered in more complex boranes.

Aluminium forms a solid polymeric hydride of formula $(Al\ H_3)_n$ by treatment of lithium hydride with aluminium chloride. The presence of excess lithium hydride leads to the formation of lithium aluminium hydride, $LiAlH_4$. Lithium aluminium hydride finds considerable use as a specific reducing agent in organic chemistry. Gallium forms compounds analogous to the borohydrides, e.g. $Li(GaH_4)$. Indium forms a polymeric hydride $(In\ H_3)_n$. There is some doubt regarding the existence of the hydride of thallium.

16.3.5 Halides

All the elements of group IIIA form trihalides MX_3. The sp^2 hybrid orbitals of boron are used in bonding and the molecules are thus planar and covalent. In gas, liquid and solid phases, boron halides exist as discrete molecular species BX_3. The boiling points of the boron halides increase as the atomic number of the halogen increases.

Boron halides are hydrolysed by water. Fluorides form fluoborates while the other halides form boric acid.

$$BF_3 + H_2O \rightarrow H\ BF_3OH$$
$$BCl_3 + 3H_2O \rightarrow B(OH)_3 + 3HCl$$
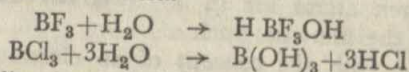
As mentioned earlier, boron halides act as electron acceptors, or Lewis acids. Boron fluoride, BF_3, is consequently used as an acid catalyst in organic reactions.

The fluorides of aluminium, gallium, indium and tellurium are ionic and have high melting points. The other halides are largely covalent when anhydrous. Aluminium halides exist as dimers, Al_2X_6, thus attaining an octet of electrons around aluminium. These dihalides have the halide-bridge structure as shown on page 531. The bridge structure is a general characteristic of electron deficient systems where the formation of bonds by electron sharing gives a nearly completed valence electron shell. The dimeric formula is retained when the halides dissolve in non-polar solvents such as benzene. When the halides dissolve in water, because of high heat of hydration, the covalent dimer is broken into $[M \cdot 6H_2O]^{3+}$ and $3X^-$ ions. Like boron fluoride, anhydrous aluminium chloride is used to catalyse many organic reactions.
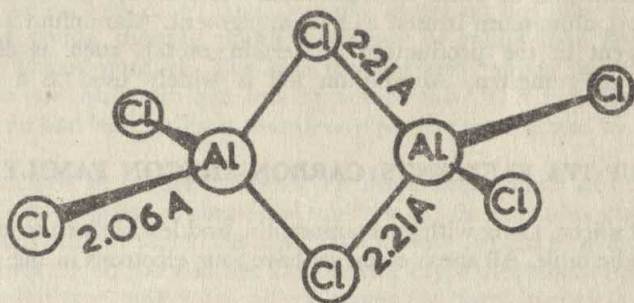
16.3.6 Other Compounds

The elements aluminium, gallium, indium and tellurium form alkoxides. The general methods of preparations of alkoxides are:

$$Al + 3ROH \xrightarrow[\text{Catalyst}]{1\% HgCl_2} (RO)_3 Al + 3/2 H_2$$

$$AlCl_3 + 3RONa \longrightarrow (RO)_3 Al + 3 NaCl$$
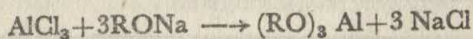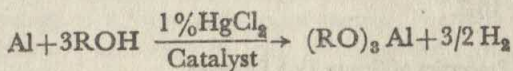
These alkoxides hydrolyse vigorously in water and are used as reducing agents for aldehydes and ketones. The alkoxides are mostly polymeric.

The elements of this group form other compounds like carbides, nitrides, phosphides, sulphides and salts of various oxyacids like sulphates, nitrates, silicates, phosphates and arsenates.

16.3.7 Occurrence, Preparation and Uses of Boron and Aluminium

These elements are never found in nature in the free state. Boron occurs in nature chiefly in the form of boric acid and its salts, such as *borax*, $Na_2B_4O_7 \cdot$ $10H_2O$. Aluminium occurs as oxides and silicates. Its chief ores are *bauxite*, *clay, kaoline, feldspar, mica, corundum* and *cryolite*. A number of gem stones contain Al_2O_3 and their colours are due to the presence of impurities such as Cr_2O_3, TiO_2, Mn_2O_3, Fe_2O_3.

Boron is usually prepared by the reduction of boric oxide with magnesium at high temperatures.

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO$$
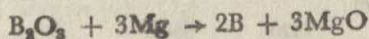
Boric oxide is obtained from borax. Boron can be isolated in reasonably pure form by reducing boron trichloride with hydrogen at a high temperature.

The chief source of aluminium is bauxite ($Al_2O_3 \cdot xH_2O$). The metal is obtained by the electroysis of alumina dissolved in fused cryolite (Na_3AlF_6) (see Fig. 12.2). Being light and a good conductor of electricity, aluminium is used for making electrical transmission cables; aluminium has thus become an effective substitute for the more expensive copper. Because of its light weight and resistance to corrosion, aluminium is used in the manufacture of household articles and reaction vessels in chemical industry. A very important use of aluminium is in the production of useful alloys like *magnalium* (Al and Mg) and *duralumin* (Al, Cu, Mg, and Mn). These alloys are light and strong and are

used in aircraft and in other transportation vehicles. In the form of finely divided flakes, aluminium is used as a paint pigment. Aluminium is used as a reducing agent in the production of certain metals such as chromium, manganese and tungsten. Aluminium foil is widely used as a wrapping material.

16.4 GROUP IVA ELEMENTS: CARBON–SILICON FAMILY

Carbon and silicon, along with germanium, tin, and lead belong to group IVA of the periodic table. All these elements have four electrons in the outermost shell.

16.4.1 General Characteristics

Carbon and silicon are typical non-metals, germanium has some metallic properties, while tin and lead are metals. Electronic configurations, ionisation energies, electronegativities and other physical properties of group IV elements are listed in Table 16.7.

Table 16.7 Physical Properties of Group IVA Elements

Property	Element				
	Carbon	Silicon	Germanium	Tin	Lead
Atomic mass	12·011	28·086	72·59	118·69	207·19
Atomic number	6	14	32	50	82
Isotopes	12, 13, 14	28, 29, 30	70, 72, 73	112, 114,	204, 206
				to 120,122,124	207, 208
Electronic structure	$2s^2 2p^2$	$3s^2 3p^2$	$3d^{10} 4s^2 4p^2$	$4d^{10} 5s^2$	$4f^{14} 5d^{10}$
				$5p^2$	$6s^2 6p^2$
Atomic radius, A	0·77	1·17	1·22	1·40	1·53
Ionic radius, M^{4+}, A	0·15	0·41	0·53	0·71	0·84
Ionisation energy, eV	I. 24·27	16·27	15·86	14·50	14·96
	II. 64·22	44·93	45·50	39·40	42·11
Electronegativity	2·50	1·90	1·70	1·70	1·60
Density, g cc^{-1}	3·52 (diamond) 2·22 (graphite)	2·49	5·36	7·30	11·34
Melting point, °C	3500	1420	958·5	231·8	327·4
Boiling point, °C	4200	2600	2700	2260	1620

The ionisation energies of these elements are rather high, necessitating extremely large amounts of energy to remove the valence electrons. Hence, there is practically no tendency for carbon and silicon to form positive ions. Nor do they show much tendency to form negative ions by gaining electrons (low electron affinity). Rather, the bonds involving these elements are covalent. In most of their compounds, group IV elements retain a valency of four; tin and lead also show divalency in several compounds. The divalent compounds are very stable. The bond energy of the $M—X$ bond ($X =$ halogen) decreases and the tetravalent state becomes somewhat unstable relative to the

divalent state with the increase of atomic mass. This explains why Pb^{2+} is more stable than Pb^{4+}.

Within the carbon-silicon family, atomic radii and densities increase while the boiling points, melting points and heats of sublimation decrease with increasing atomic number. The high melting and boiling points of carbon and silicon are quite unique among non-metals. The reduction potential values for tin and lead indicate that these elements are oxidised by hydronium ion.

As mentioned in earlier chapters, an important feature of carbon is its ability to form a variety of single and multiple bonds with other carbon atoms. Silicon atoms can also form covalent links with one another to a limited extent, but the bonds are not very stable. Double and triple bonds between two silicon atoms are, however, unknown. Silicon atoms can form long chains and rings when alternated with oxygen atoms, as in the simple and complex silicates. Silicon bonds are also predominantly covalent (and tetrahedral) like those of carbon, but possess appreciable ionic character compared to the corresponding carbon bonds.

Both carbon and silicon are rigid solids which may be thought of as giant molecules consisting of a large number of atoms. The element silicon has the same crystal structure as diamond, each silicon atom forming single covalent bonds with four adjacent silicon atoms which surround it tetrahedrally.

16.4.2 Allotropic Modifications

Carbon occurs in two well-defined crystalline forms (graphite and diamond) whereas silicon is available in only one crystalline form. Graphite is a soft black substance with a greasy touch, while diamond is a colourless transparent sparkling solid. Diamond is the hardest substance known. It is interesting to note that diamond is thermodynamically less stable than graphite at ordinary temperatures, but the activation energy being very high, the rate of the diamond transformation to graphite is very slow (see Chapters 10 and 13). Silicon exists only in the diamond structure. It is also a non-conductor and is hard. Tin exists in three modifications:

$$\alpha\text{-Sn} \xrightarrow{11°C} \beta\text{-Sn} \xrightarrow{169°C} \gamma\text{-Sn}$$
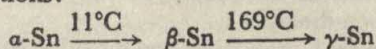
α-Tin has the diamond type structure, β-Sn has a cubic closed packed structure and γ-Sn has simple cubic metallic structure. Lead has only one modification having cubic structure. This tendency of elements to exist in more than one molecular form is called *allotropism*. Other examples of allotropism are phosphorus and oxygen (O_2, O_3).

16.4.3 Oxides

Carbon is a non-metal and its oxide is weakly acidic; silicon is slightly more metallic and its oxide is more basic. Germanium, tin and lead are increasingly metallic and their oxides are increasingly basic in character. The most common oxides of these elements have the composition MO_2 where M represents an element of this group. Though carbon dioxide and silicon dioxide have similar formulae, they have vastly different properties. Carbon dioxide is a gas at ordinary temperatures whereas silicon dioxide is a hard network solid. This is due to the difference in the structure of these compounds. Carbon dioxide is a non-polar linear molecule with two double bonds. The intermolecular forces

in carbon dioxide are the weak van der Waals forces. Even in the crystalline state, carbon dioxide is found to consist of individual carbon dioxide molecules held together by weak forces (see Chapter 7). Silicon dioxide, on the other hand, is characterised by single bonds. A crystal of silicon dioxide does not contain individual SiO_2 molecules; instead, it consists of a continuous lattice of silicon and oxygen atoms connected by covalent bonds. In this lattice each silicon atom is tetrahedrally surrounded by four oxygen atoms, and each oxygen atom is bonded to two silicon atoms (Fig. 16.5) and the entire crystal of silicon dioxide may be considered to be a giant molecule, or a *macromolecule*.
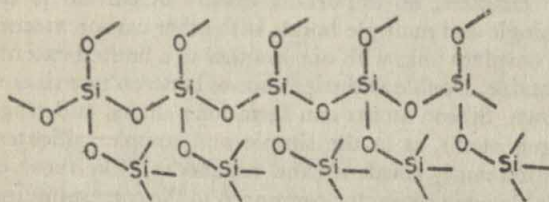
Fig. 16.5 Macromolecular structure of silica

Carbon dioxide reacts with water to give a weakly acidic solution of carbonic acid.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
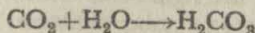
Carbonic acid is responsible for the sour taste of carbonated drinks. Silicon dioxide is insoluble in water. It dissolves in hot sodium hydroxide solution forming sodium silicate.

$$SiO_2 + 4NaOH \longrightarrow Na_4SiO_4 + H_2O$$
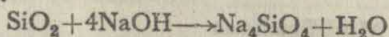
Carbon monoxide, CO, another oxide of carbon, has the largest bond energy among diatomic molecules (256 kcal mol^{-1}). It has a triple bonded carbon atom with one σ- and two π-bonds. It is a powerful electron donor and reacts with electron deficient compounds like B_2H_6 to form stable molecules. Thus,

$$2CO + B_2H_6 \longrightarrow 2OC : BH_3$$
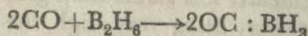
Carbon monoxide forms coordination compounds with most of the transition metal ions, e.g. $Ni(CO)_4$. In most such compounds, carbon monoxide stabilises the low oxidation state of the metal. Carbon monoxide readily reacts with oxygen to form carbon dioxide.

Tin and lead form both monoxides and dioxides. SnO and SnO_2 are slightly amphoteric and form stannites and stannates. However, PbO is basic while PbO_2 is a powerful oxidising agent. Germanium forms GeO_2 which is weakly acidic. All these oxides are formed by the direct combination of the elements.

Silicon dioxide or silica, SiO_2, occurs in nature in various crystalline forms— *quartz* (which is most widespread), *cristobalite* and *tridymite*. Quartz occurs in many deposits as well-formed crystals. It is also the crystalline constituent of many rocks such as granite. It is a hard colourless solid. It is transparent to ultraviolet rays, whereas ordinary glass is opaque. Hence, quartz is used in many optical instruments where short wavelength transparency is necessary.

If any form of silica is melted (m.p. about 1600°C) and the molten mass cooled, it usually does not crystallise at the original melting point. The liquid becomes more and more viscous as the temperature is lowered. At about 1500°C, it becomes so viscous that it does not flow. Such a supercooled liquid is called *silica glass* (or sometimes quartz glass or fused quartz). Because of its low co-efficient of expansion, silica glass is used in making apparatus which can with-

stand relatively high temperatures; red-hot silica glass may even be immersed in water without cracking.

16.4.4 Hydrides

All group IVA elements form covalent hydrides of the type MH_4. The number of hydrides and the ease of their formation decreases from carbon to lead. Carbon forms a vast number of hydrides (hydrocarbons). Silicon forms a limited number of saturated hydrides called silanes of the general formula Si_nH_{2n+2}. Mono-silane, SiH_4, is a colourless, stable (but readily flammable) gas consisting of non-polar covalent (tetrahedral) molecules. Other known silicon hydrides are: Si_2H_6, Si_3H_8, Si_4H_{10}, Si_5H_{12} and Si_6H_{14}. Notice the similarity of these formulae to those of alkanes, C_nH_{2n+2}. Silicon hydrides are much more reactive than the alkanes. They are strong reducing agents, burn in air, explode in chlorine and are readily hydrolysed by alkaline solutions. This is because silicon-silicon bonds and silicon-hydrogen bonds are weaker than the corresponding carbon-carbon and carbon-hydrogen bonds in alkanes.

16.4.5 Halides

Group IVA elements form tetrahalides of the type MX_4 (X=halogen), which are tetrahedral and covalent. Tetrachlorides are highly volatile liquids. With the exception of carbon tetrachloride, all other chlorides are hydrolysed by water to hydrochloric acid and an oxy-acid.

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$$
$$\text{(silicic acid)}$$
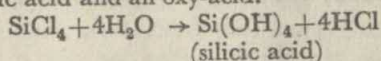
Carbon and silicon also form chloroforms of the formula $MHCl_3$ and oxy-chlorides of the formula $MOCl_2$.

The ability of group IVA elements to form complexes is favoured by a high charge, small size and availability of empty orbitals of the right energy. The quadrivalent compounds of carbon possess the closed shell electronic configuration of a noble gas and therefore carbon does not form complexes. Silicon, however, can form complexes due to the availability of d orbitals, and a coordination number of six is found in these complexes. For example, in the formation of $[SiF_6]^{2-}$ from SiF_4, four covalent and two coordinate bonds are formed as a result of sp^3d^2 hybridisation (which imparts an octahedral structure to the compound formed).

16.4.6 Silicates

Silicate is the general term given to solids with silicon-oxygen bonds. Most of the minerals that constitute rocks and soil are silicates. The only soluble silicates are those of alkali metals. Sodium silicate, Na_4SiO_4, is usually solid in the form of its concentrated aqueous solutions, known as *water glass*. It is used for fire-proofing wood and cloth, as an adhesive and for preserving eggs. Ordinary glass is a super-cooled liquid which is obtained by fusing a mixture of sand, sodium carbonate and calcium carbonate.

The commercial importance of silicates lies in their use for the manufacture of pottery, glass, enamels and cement. Some of the important silicate minerals are listed below.

Feldspar	Potassium aluminium silicate,	$KAlSi_3O_8$
Chabazite	Hydrated calcium aluminium silicate,	$CaAl_2Si_4O_{12}.6\ H_2O$
Diopside (asbestos)	Calcium magnesium silicate,	$CaMgSi_2O_6$

Silicates are complex network solids. Planar sheet structures with weak van der Waals forces between layers are present in some silicates, while in others infinite three-dimensional structures are obtained. Figs. 16.6–16.8 illustrate the structures of several silicate polymers.
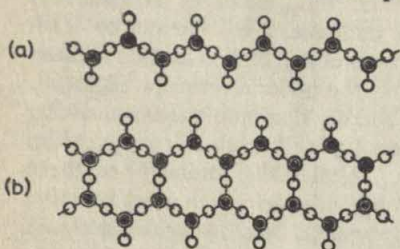
Fig. 16.6 Chain structures of silicate minerals: (*a*) pyroxenes and (*b*) amphiboles
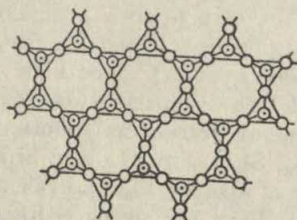
Fig. 16.7 Sheet structure of silicates such as mica
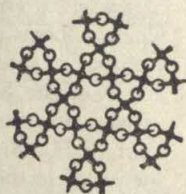
Fig. 16.8 Structure of quartz

16.4.7 Silicones

Elemental silicon which has been alloyed with copper reacts with alkyl halides producing alkyl halosilanes. In this reaction copper acts as a catalyst. The Si—O bonds in alkylhalosilanes are very stable, but the Si—Cl bonds undergo hydrolysis whereby the chlorine atoms are replaced by OH groups.

(Methyl chloride)
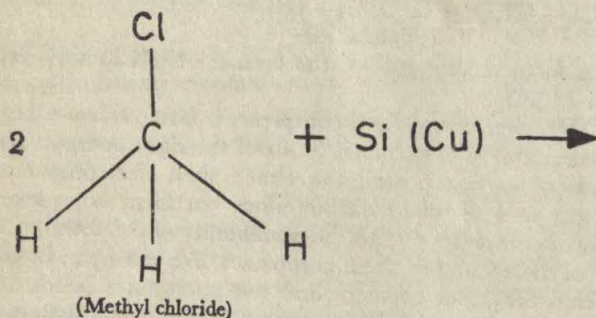
As soon as the Si—OH bonds are formed by hydrolysis, condensation sets in with the elimination of water. These types of polymeric silicon-oxygen compounds are called *silicones*.* By regulating the conditions of the reactions, the condensation process can be stopped at any stage and rings of various sizes or chains of desired lengths can be produced. Further, by choosing a certain proportion

(Methyl chlorosilane)
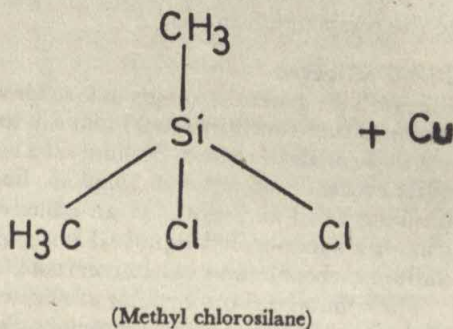
of methyl silicon trichloride, a desired number of cross links can be formed between chains. Thus, silicone products having the physical properties of oils,

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*The empirical formula for these compounds is approximately $(CH_3)_2SiO$, which is similar to the formula of acetone, $(CH_3)_2CO$, and hence the name silicone.
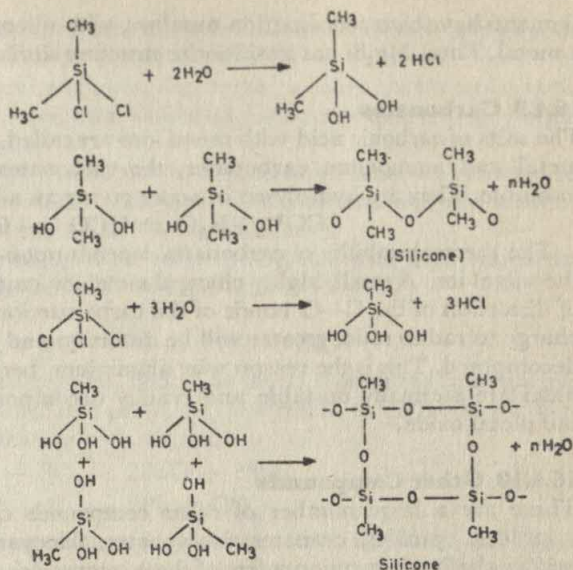
Fig. 16.9 Preparation and structures of silicones

plastics, resins, etc., are produced. Chemically, silicones are inert, water-repellent, heat-resistant and good electric insulators. These properties make these compounds useful as protective coating, lubricants, insulators, etc. A whole new field of chemistry and technology, civilian as well as military, has been opened by the development of silicones in the last two or three decades.

16.4.8 Carbides and Silicides

Generally, carbides are formed by the union of carbon with the metals or their oxides at high temperatures. They can also be prepared by heating the metal in the vapour of a suitable hydrocarbon,

$$xC + yM \rightarrow M_yC_x$$
$$2Na + HC \equiv CH \rightarrow Na_2C_2 + H_2$$
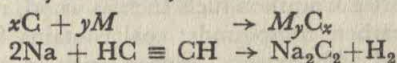
The carbides are generally classified into three types: (*i*) ionic, (*ii*) covalent, and (*iii*) interstitial. In ionic carbides, carbon is present in the form of methanide or acetylide ions, C^{4-} or $(C=C)^{2-}$ ions and the metals are present as metal ions (e.g. Be_2C, Na_2C_2). Carbides are hydrolysed to give either methane or acetylene depending on the nature of the carbide.

Covalent carbides are hard, infusible and inert. They are formed either by heating boron or silicon with carbon. They are giant molecules having diamond structures.

In interstitial carbides, carbon atoms are present in the spaces between the metallic atoms giving a slightly expanded metallic lattice. Examples of this type of carbides are TiC, ZrC, MoC and WC. They have the rock-salt structure and are extremely hard; they are good electrical conductors, and have high melting points, and are not hydrolysed. Iron, manganese and chromium also form interstitial type of carbides where carbon is present in the form of C—C—C chains. Silicon forms binary compounds with a number of metals to yield silicides. Typical examples of silicides are Cu_5Si, $CaSi_2$, $ThSi_2$, V_3Si, $MnSi$, $CoSi$, and $NiSi$. Most of them have typical alloy structures in which both

elements have high coordination numbers, with silicon behaving essentially like a metal. Thus, Mg_2Si has antifluorite structure similar to Mg_2Sn or Mg_2Pb.

16.4.9 Carbonates

The salts of carbonic acid with metal ions are called carbonates. Except alkali metal and ammonium carbonates, the carbonates of all other metals are insoluble. They are hydrolysed in water giving an alkaline solution:

$$CO^{2-}_3 + H_2O \rightleftharpoons HCO^-_3 + OH^-$$
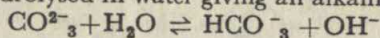
The thermal stability of carbonates depends upon the size and the charge of the metal ion. A small, highly charged metal ion causes a considerable amount of distortion of the C—O bonds of the carbonate ion. The higher the value of charge to radius ratio, greater will be distortion and more easily the carbonate decomposed. This is the reason why aluminium, beryllium and lithium carbonates are thermally unstable and readily decompose to carbon dioxide and the metal oxide.

16.4.10 Other Compounds

There are a large number of other compounds of these elements such as sulphides, cyanides, cyanates, isocyanates, thiocyanates and isothiocyanates, but we shall only mention a few of these compounds here. Generally, sulphides are prepared by the direct union of sulphur with the elements. CS_2 is a liquid, while others are solids. CS_2 is a linear molecule like CO_2. SiS_2 and GeS_2 consist of long chains. Tin and lead form monosulphides which are soluble in ammonium sulphide giving thiosalts. Oxy-salts of germanium, tin, and lead are prepared by the reaction of the respective oxy-acid with the metallic oxide or metal ion [e.g. $PbSO_4$, $Pb(NO_3)_2$].

16.4.11 Occurrence, Properties and Uses

Although carbon occurs in the earth's crust only to the extent of about 0·03 per cent, the element is of great importance because of its presence in animal and vegetable matter. Common fuels such as wood, natural gas and petroleum contain mostly carbon compounds; coal contains free as well as combined carbon. Combined with oxygen, carbon exists in the atmosphere as carbon dioxide. Large deposits of carbonates, particularly those of calcium and magnesium are found in the earth's crust. In the free state carbon occurs to a slight extent as diamond and graphite, its two crystalline allotropic forms.

Diamonds are used in industry for making very hard abrasive powders and for grinding wheels and the tips of drills and saws. Graphite is used as the black constituent in ordinary pencil leads, as the pigment in black paints, in the manufacture of crucibles and electrodes to be used at extremely high temperatures, and as a dry lubricant.

Silicon is the second most abundant element after oxygen, and is found in a variety of silicate minerals. As silica, SiO_2, it occurs in *sand, flint* and *quartz*.

Elemental silicon, Si, can be prepared by heating SiO_2, at very high temperature with a reducing agent, such as carbon, or with an electropositive metal (Mg or Al). Silicon is used in the electronics industry for the manufacture of transistors. Silicon forms alloys with metals like copper and iron. Iron-silicon alloy known as ferrosilicon is used in the steel industry, both as a 'scavenger' to remove dissolved gases from steel as well as an alloying element. Steel containing silicon to the extent of 14 per cent is highly resistant to corrosion

by air or acids. Silicon is added to a number of non-ferrous alloys to bring about desirable modifications in their properties. Sand finds use in construction work, in the manufacture of cement and glass. *Rock crystal*, a colourless form of quartz is used for making optical apparatus. Coloured varieties of quartz (e.g. purple *amethysts*) are valued as gems.

Germanium, tin, and lead, in contrast to carbon and silicon, are rather rare elements. Tin and lead are easily recovered from their ores and are technologically important as pure metals and in form of alloys.

The only important ore of tin is the oxide SnO_2, *cassiterite*, from which tin can be obtained by heating the oxide with carbon in a furnace.

$$SnO_2 + 2C \xrightarrow{\text{heat}} 2CO + Sn$$
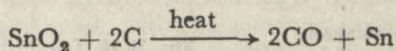
The common ore of lead is *galena*, PbS. The metal is produced from galena by roasting the ore in air until it is completely converted to the oxide and the oxide is then reduced by heating with carbon.

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$2PbO + C \rightarrow 2Pb + CO_2$$
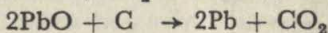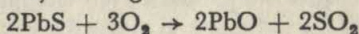
The principal source of germanium is *sphalerite*, a zinc sulphide (ZnS) ore, which contains only about 1 per cent of germanium as the sulphide. The extraction of germanium from its sulphide ore is similar to the process that is used in extracting lead. Germanium is used in the electronics industry for the manufacture of transistors.

Tin is used for preparing alloys while tin amalgam is used for silvering mirrors. The metal along with an acid is an important reducing agent. It is used for tinning copper and brass utensils to prevent poisoning of food. It is employed for plating of iron to prevent rusting.

Lead tetraethyl, Pb $(C_2H_5)_4$, is a commercially important compound owing to its 'antiknock' properties when added to petrol. Other important commercial uses of lead are in the manufacture of lead storage batteries and the production of *white lead*, $2PbCO_3 \cdot Pb(OH)_2$, which is used as a pigment in paints.

16.5 GROUP VA ELEMENTS: NITROGEN FAMILY

The elements—nitrogen, phosphorus, arsenic, antimony, and bismuth—in group VA of the periodic table constitute the nitrogen family. They are similar to one another in some respects, but they also show prominent differences (Table 16.8). The transition from non-metallic to metallic character within this group is more noticeable than in other groups. As elsewhere, the first element of this group is somewhat unique, whereas the remaining elements in the family show greater similarity towards each other.

16.5.1 General Characteristics

The electronic configuration of the elements of the nitrogen family is [core] ns^2np^3 (Table 16.8). The elements of this group have five electrons in their outermost shell. Nitrogen and the phosphorus atoms, being small and relatively more electronegative, accept three electrons to form nitrides and phosphides (e.g. Li_3N and Ca_3P_3). The heavier elements of this group, however, tend to give away their outermost electrons to form M^{5+} or M^{3+} ions. This tendency of

the lighter elements to gain electrons and the heavier elements to lose electrons (in order to complete their octet) displays the transition from non-metallic to metallic behaviour. All the group VA elements have a great tendency to form covalent bonds as evidenced by the examples in Fig. 16.10.
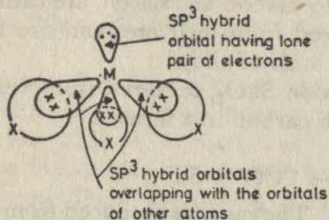
Fig. 16.10 Tetrahedral structure of MX_3 type molecules. (X=halogen, and M=group VA element)
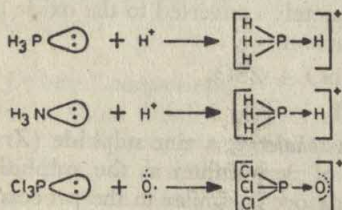
The heavier elements of VA group have empty d orbitals available for bond formation. They can utilise sp^3d and sp^3d^2 hybridised orbitals to form compounds with trigonal bipyramid (or square pyramid) and octahedral structure respectively [e.g. PCl_5, $(PCl_6)^-$ shown in Fig. 16.11].
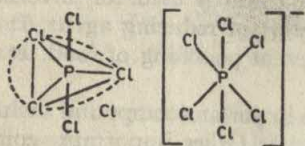
Fig. 16.11 Structure of PCl_5 and PCl_6^- ion

Like carbon (and to some extent silicon), nitrogen has a great tendency to form multiple bonds; this tendency decreases rapidly as we go down the group. Arsenic, antimony and bismuth do not form any compound in which they exhibit multiple bonds.

Table 16.8 Physical Properties of Group VA Elements

Property	Element				
	Nitrogen	*Phosphorus*	*Arsenic*	*Antimony*	*Bismuth*
Atomic mass	14·0067	30·9738	74·9216	121·75	208·980
Atomic number	7	15	33	51	83
Isotopes	14, 15	31	75	121, 123	209
Electronic structure	$2s^22p^3$	$3s^23p^3$	$3d^{10}5s^24p^3$	$4d^{10}5s^2$ $5p^3$	$4f^{14}5d^{10}$ $6s^26p^3$
Atomic radius, A	0·70	1·10	1·21	1·41	1·52
Ionic radius, A	1·71 (N^{3-})	2·12 (P^{3-})	2·22 (As^{3-})	0·62 (Sb^{5+})	0·74 (Bi^{5+})
Electronegativity	3·07	2·06	2·00	1·82	1·67
Ionisation energy, eV	47·42	30·15	28·0	24·7	25·4
Density, g cc^{-1}	0·96 (solid)	1·82 (white)	5·72 (grey)	6·69	9·80
Melting point, °C	−210	44·1 (white)	817 (grey)	630·5	271
Boiling point, °C	−195·8	280	633	1375	1560

The elements of this group exhibit a maximum oxidation state of five towards oxygen by using all the five outer electrons in forming bonds. As the atomic number increases, there is an increasing tendency for the paired s electrons to remain inert, and only the p electrons are used in bonding giving rise to trivalency. Valencies of 3 and 5 are shown in compounds with halogens and with sulphur. The hydrides are trivalent. In the case of nitrogen, a wide range of oxidation states exist from -3 to $+5$; $NH_3(-3)$; $N_2H_4(-2)$; $NH_2OH(-1)$; $N_2(0)$; $N_2O(+1)$; $NO(+2)$; $N_2O_3(+3)$; $NO_2(+4)$; N_2O_5 and $HNO_3(+5)$.

At ordinary temperatures, nitrogen is a gas; phosphorus is a soft, waxy and lustreless solid; arsenic is a hard solid with slight metallic lustre; and antimony and bismuth are hard solids with characteristic metallic lustre. Arsenic and antimony are brittle and can be powdered, while bismuth is comparatively less brittle. The atomic size increases steadily as the atomic number increases within this group and the ionisation energy decreases in the series. This trend in ionisation energy suggests the increasing electropositive or metallic character. The electronegativities show that nitrogen has a high electron affinity and that the affinity decreases down the family. Electrical conductivity increases gradually from nitrogen to bismuth. Nitrogen and phosphorus are non-conductors; arsenic is a poor conductor, antimony is a good conductor and bismuth, an excellent conductor of electricity. There is a pronounced increase in hardness and density in going from phosphorus to bismuth.

16.5.2 Allotropic Modifications

Phosphorus exists in three allotropic modifications: (*i*) white phosphorus, (*ii*) red phosphorus, and (*iii*) black phosphorus. White phosphorus is a molecular solid of tetrahedrally arranged P_4 units; red phosphorus has a complex chain
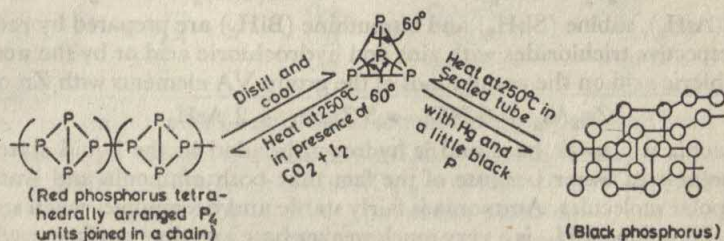
Fig. 16.12 Allotropes of phosphorus and their interconversions

structure; black phosphorus has a structure made up of layers of phosphorus atoms. The structures and the conditions for interconversion amongst them are given in Fig. 16.12. This is the reason for the reactivity and low volatility of white phosphorus. The P—P—P bond angle of 60° in white phosphorus indicates considerable strain. This strain is removed in red phosophorus and in black phosphorus because bonds break and cross linking occurs giving almost strainless hexagonal rings in black phosphorus with P—P—P bond angles of about 100°. Arsenic and antimony also exist as yellow varieties with tetrahedral As_4 and Sb_4 structures; black arsenic and antimony have structures similar to black phosphorus. Nitrogen and bismuth do not occur in allotropic modifications.

16.5.3 Hydrides

All the elements of this group form volatile hydrides of the formula MH_3. The hydrides are colourless gases and show regular trends in properties. The structure of these hydrides is described as pyramidal or tetrahedral with one position occupied by a lone pair. The heat of formation of the hydrides decreases from NH_3 to SbH_3.

Industrially, ammonia is manufactured by the well-known *Haber process* (see Chapter 10).

$$N_2 + 3H_2 \rightleftharpoons 2\,NH_3$$
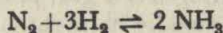
This reaction is very slow and no ammonia is formed when nitrogen and hydrogen gases are mixed at room temperature. At high temperatures and in the presence of a catalyst (e.g. iron), the rate of reaction becomes appreciably high. Since the reaction is exothermic, the equilibrium constant at elevated temperatures ($>450°C$) is smaller. The unfavourable equilibrium constant at high temperature is counteracted by carrying out the reaction at high pressures (about 1000 atm). This increases the yield of the product due to the decrease in the total volume of products with respect to that of reactants.

The cyanamide process of the manufacture of ammonia involves the following reaction:

$$CaC_2 + N_2 \xrightarrow{\quad 1100°C \quad} CaCN_2 + C$$
$$CaCN_2 + 3\,H_2O \longrightarrow CaCO_3 + 2\,NH_3$$
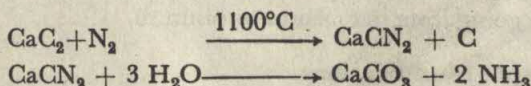
Phosphine is prepared by the reaction of sodium hydroxide with white phosphorus or by the hydrolysis of calcium phosphide.

$$P_4 + 3\,NaOH + 3\,H_2O \rightarrow 3\,NaH_2PO_2 + PH_3$$
$$Ca_3P_2 + 6\,H_2O \rightarrow 3\,Ca(OH)_2 + 2\,PH_3$$
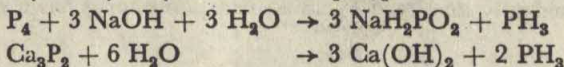
Arsine (AsH_3), stibine (SbH_3) and bismuthine (BiH_3) are prepared by reducing their respective trichlorides with zinc and hydrochloric acid or by the action of hydrochloric acid on the compounds of the group VA elements with Zn or Mg.

$$Zn_3As_2 + 6\,HCl \rightarrow 3\,ZnCl_2 + 2\,AsH_3$$
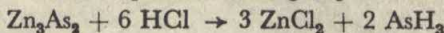
Ammonia is a weak base and is hydrogen-bonded in the liquid state. It is freely soluble in water because of the fact that both ammonia and water are strong polar molecules. Ammonia is fairly stable and decomposes when strongly heated. Phosphine, PH_3, is a very much weaker base and does not form hydrogen bonds. It is insoluble in water and is easily decomposed by heat. AsH_3, SbH_3 and BiH_3 are insoluble in water and have no basic properties. Arsine is easily decomposed by heat; stibine decomposes explosively when heated and bismuthine decomposes spontaneously at room temperature. Thus, we notice that the polarity of the M—H bond in the hydrides decreases with the decrease in the electronegativity; the hydrides become decreasingly stable and less basic with rise of atomic number. The stability of these hydrides is also indicated by their decomposition temperature and bond energies.

The hydrides of group VA elements are strong reducing agents:

$$PH_3 + 3\,OH^- \rightleftharpoons P + 3\,H_2O + 3e^- \qquad (E°_{red} = -\,0·89\ V)$$
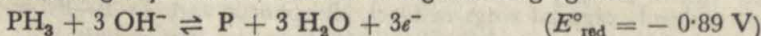
They react with metal ions to give phosphides, arsenides, and stibnides. They are inflammable and poisonous. Ammonia is a base and accepts protons from water.

$$NH_3 + H_2O \rightleftharpoons NH^+_4 + OH^-$$
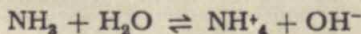
However, this equilibrium is well over to the left-hand side and solutions of NH_3 in water contain few NH^+_4 ions; ammonia is present as $NH_3(aq)$ where ammonia is hydrogen-bonded to water molecules.
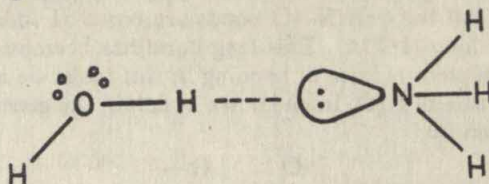
With good proton donors like hydrochloric acid, ammonia forms NH^+_4 salts and utilises the lone pair of electrons on nitrogen. Phosphine forms salts with hydrochloric and hydroiodic acids only under anhydrous conditions. Some of the other hydrides of group VA elements are hydrazine (N_2H_4), hydroxylamine (NH_2OH), hydrazoic acid (N_3H), and diphosphine (P_2H_4).

16.5.4 Oxides

Oxides of nitrogen and their properties are given in Table 16.9. Some of the

Table 16.9 Properties of the Oxides of Nitrogen

Oxide	Oxidation state	Physical state	Colour	Melting point, °C	Boiling point, °C
N_2O	+1	Gas	Colourless	−99	−88
NO	+2	Gas	Colourless	−164	−152
N_2O_3	+3	Solid at low temp.	Blue	Decomposes at 27°C	3·5
N_2O_4	+4	Gas	Colourless	−9·0	21
NO_2	+4	Gas	Brown	—	—
N_2O_5	+5	Gas	Colourless	30	47

reactions by which the various oxides of nitrogen are prepared are listed below:

$$NH_4NO_3 \rightleftharpoons N_2O + 2H_2O \text{ (NITROUS OXIDE)}$$
$$8\,HNO_3 + 3\,Cu \rightleftharpoons 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO \text{ (NITRIC OXIDE)}$$
$$2NO + O_2 \rightarrow 2NO_2 \text{ (NITROGEN DIOXIDE)}$$
$$2\,NO_2 \rightleftharpoons N_2O_4 \text{ (DINITROGEN TETROXIDE)}$$
$$NO + NO_2 \rightarrow N_2O_3 \text{ (NITROGEN TRIOXIDE)}$$
$$2\,HNO_3 + P_2O_5 \rightleftharpoons 2\,HPO_3 + N_2O_5 \text{ (NITROGEN PENTOXIDE)}$$
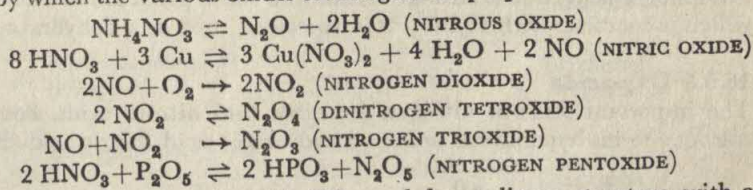
Nitrous oxide is isoelectronic with CO_2 and has a linear structure with a dipole moment of 0·16 debye. This suggests that N_2O has contributions from the following resonance forms:

$$[:\overset{-}{N}=\overset{+}{N}=\overset{..}{O}:] \longleftrightarrow [:N \equiv \overset{+}{N} - \overset{\overline{..}}{O}:]$$
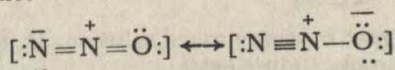
Nitric oxide has an odd number of electrons. It is paramagnetic with a N—O bond distance 1·14 A which is in between double and triple bond distances (see Chapter 4 also).

Nitrogen dioxide (NO_2) is also an odd-electron paramagnetic molecule. Its properties like colour, and ready dimerisation to colourless and diamagnetic N_2O_4 are what one should expect from an odd-electron molecule. The molecule

is non-linear with O—N—O angle 134°, stabilised by reasonating structures. It can lose its odd electron fairly readily to give the nitronium ion (NO^+_2). Dinitrogen tetroxide, N_2O_4, is the dimer of NO_2. It is a planar molecule having four N—O bonds. All the four N—O bonds are equal (1·18A) but the N—N bond is unusually long (1·75A). This long bond has been associated with the π-bond but the complete picture of bonding in this molecule is not very clear. Although the structure of N_2O_5 is not known in detail, the general arrangement of the atoms is given by,

$$
\begin{array}{cc}
O- & O- \\
| & | \\
+N—O—N^+ \\
\| & \| \\
O & O
\end{array}
$$
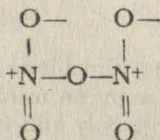
In the solid state, N_2O_5 is thought to exist as $NO^+_2NO^-_3$ (nitronium nitrate). The oxides NO_3 and N_2O_6 have been reported as products of the reaction of ozone with N_2O_5, but have not been isolated.

The other elements of the group form the following oxides: P_4O_6, As_4O_6, Sb_4O_6, Bi_2O_3, P_4O_{10}, and Sb_4O_{10}. Phosphorous oxide, P_4O_6, is prepared by passing a slow stream of air over red phosphorus at 60°C. Arsenous and antimonous oxides (As_4O_6) and (Sb_4O_6) are prepared by heating the elements in air; and bismuth oxide (Bi_2O_3) by the thermal decomposition of bismuth nitrate. Phosphoric oxide (P_4O_{10}) is usually obtained by burning white phosphorus in excess of air or oxygen while arsenic and antimony pentoxides are obtained by carefully dehydrating arsenic and antimonic acids (H_3AsO_4, H_3SbO_4) respectively.

Phosphorous oxide is strongly acidic and is highly soluble in water; in water it gives phosphorous acid (H_3PO_3) which on warming gives orthophosphoric acid (H_3PO_4). Arsenous and antimonous oxides are amphoteric and sparingly soluble in water. They produce arsenite (AsO_2)$^-$ and antimonite (SbO_2)$^-$ ions. Bismuth oxide is predominantly basic and dissolves in acids.

$$As_4O_6 + 4OH^- \rightarrow 4\,AsO_2^- + 2H_2O$$
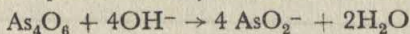
Phosphorus pentoxide is strongly acidic and has a great affinity for water with which it combines with H_3PO_4 It is, therefore, used as a dehydrating agent.

16.5.5 Oxy-acids
The important acids of nitrogen are nitric and nitrous acids. Besides these, nitrogen forms hyponitrous acid and hydroazoic acid. Nitric acid (Fig. 16.13)
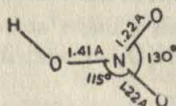
Fig. 16.13 Structure of nitric acid

is a strong oxidising agent in concentrated solution. It, therefore, reacts with metals like copper to produce nitric oxide:

$$3\,Cu + 2\,NO^-_3 + 8\,H^+ \rightarrow 3\,Cu^{2+} + 2\,NO + 4\,H_2O$$
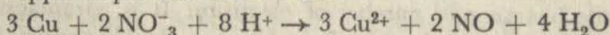
Its oxidising power decreases with dilution. Thus, the reaction of $2M$ HNO_3 with metals gives hydrogen gas. The decrease in the oxidising strength with dilution may be understood as follows. According to the reaction,

$$NO^-_3 + 4H^+ + 3e^- \rightleftharpoons NO + 2H_2O \qquad (E^\circ_{red} = 0.96\ V)$$
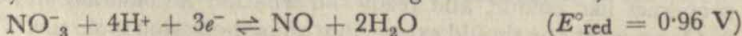
the oxidising power of NO^-_3 is very sensitive to H^+. Higher the concentration

of H⁺ and NO⁻₃ ions, higher will be the oxidising power. Thus, a higher concentration of nitric acid will increase the oxidising power. The following half-reactions illustrate how the products vary with acid concentration:

$$\text{(i)} \quad NO_3^- + 2\,H^+ + e \rightarrow H_2O + NO_2 \qquad E^\circ = 0\cdot80\ V$$
$$\text{(ii)} \quad NO_3^- + 4\,H^+ + 3\,e \rightarrow NO + 2H_2O \qquad E^\circ = 0\cdot96\ V$$
$$\text{(iii)} \quad NO_3^- + 6\,H^+ + 5\,e \rightarrow \tfrac{1}{2}N_2 + 3H_2O \qquad E^\circ = 1\cdot25\ V$$
$$\text{(iv)} \quad NO_3^- + 7\,H^+ + 6\,e \rightarrow NH_2OH + 2H_2O \quad E^\circ = 0\cdot96\ V$$
$$\text{(v)} \quad NO_3^- + 10\,H^+ + 8\,e \rightarrow NH_4^+ + 3H_2O \qquad E^\circ = 0\cdot88\ V$$
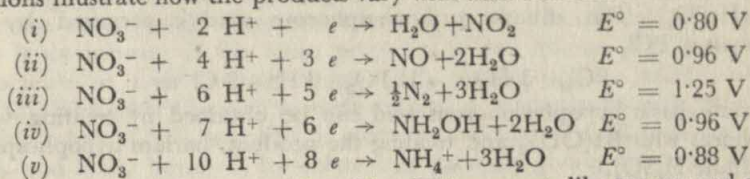
Reactions (*i*) and (*ii*) occur with mild reducing agents like copper and silver, while the other reactions occur with stronger reducing metals, like iron, tin and manganese. In these reactions, the metal provides electrons.

$$Cu \rightarrow Cu^{2+} + 2e$$
$$2\,NO_3^- + 4\,H^+ + 2e \rightarrow 2\,NO_2 + 2\,H_2O$$
$$\overline{Cu + 2\,NO_3^- + 4\,H^+ \rightarrow Cu^{2+} + 2\,NO_2 + 2\,H_2O}$$
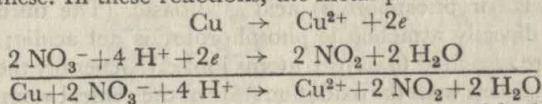
Aqua-regia is a mixture of three parts of concentrated hydrochloric acid and one part of concentrated nitric acid. The following reaction takes place on mixing the two acids.

$$3\,HCl + HNO_3 \rightarrow NOCl + Cl_2 + 2\,H_2O$$
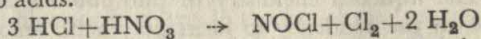
It is the presence of NOCl and Cl_2 which makes aqua-regia a powerful oxidising agent. Aqua-regia dissolves metals like platinum to form halides, e.g. $[PtCl_6]^{2-}$.

Nitrous acid is a weak acid $(K = 4\cdot5 \times 10^{-4})$. The pure liquid acid is unknown. In gaseous phase it dissociates as

$$2\,HNO_2(g) \rightleftharpoons NO(g) + NO_2(g) + H_2O \qquad (K = 0\cdot57)$$
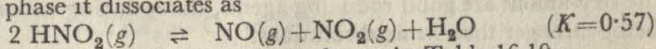
Phosphorus forms a number of oxy-acids, as shown in Table 16.10.

Table 16.10 Oxy-acids of Phosphorus and their Structures

Formula	Name and oxidation state of Phosphorus	Structure	Remarks
H_3PO_2	(Hypophosphorous) +1	O=P with H, OH, H	Tetrahedral (monoprotic)
H_3PO_3	(Orthophosphorous) +3 (Phosphorous)	O=P with H, OH, OH	Tetrahedral (diprotic)
$(HPO_3)_n$	(Metaphosphoric) +5	O=P—OH chains with O bridges	Long chains of PO_4 tetrahedral (monoprotic)
H_3PO_4	(Orthophosphoric) +5 (Phosphoric)	O=P with OH..., OH..., OH...	Tetrahedral molecules highly hydrogen bonded (triprotic)
$H_4P_2O_7$	(Pyrophosphoric) +5	HO—P, P—OH with O, HO, OH	Two PO_4 tetrahedral linked through oxygen bridge (tetraprotic)

Metaphosphoric acid is formed when a small amount of water is added to P_4O_{10}. This is a polymeric material as shown in Table 16.10. Further addition of water gives first pyrophosphoric acid ($H_4P_2O_7$) and then, orthophosphoric acid (H_3PO_4). The dibasic, orthophosphorous acid is prepared by the hydrolysis of PCl_3.

$$PCl_3 + 3 H_2O \rightarrow H_3PO_3 + 3 H^+ + 3 Cl^-$$
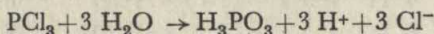
The mono-basic hypophosphorous acid can be obtained by treating white phosphorus with $Ba(OH)_2$ and treating the product, barium hypophosphite, with dilute H_2SO_4.

$$2 P_4 + 3 Ba(OH)_2 + 6 H_2O \rightarrow 2 PH_3 + 3 Ba(H_2PO_2)_2$$
$$3 Ba(H_2PO)_2 + 3 H_2SO_4 \rightarrow 3 BaSO_4 + 6 H_3PO_2$$
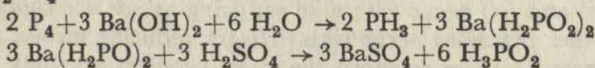
Orthophosphorous (or phosphorous) acid is dibasic. (The third hydrogen atom in this acid, directly attached to phosphorous, is not acidic; only those hydrogens which are attached to oxygen atoms ionise.) Generally the ionisation constants of acids increase with the oxidation state of the central atom. However, this is not so with H_3PO_2, H_3PO_3 and H_3PO_4 ($K_1 = 10^{-2}$, $K_1 = 1.6 \times 10^{-2}$, $K_1 = 6 \times 10^{-3}$ respectively) because of the peculiar structures of hypo- and ortho-phosphorous acids. The aqueous chemistry of phosphorous and phosphoric acids is complex due to the tendency to form polymeric anions in aqueous solution.

Phosphorus exists in a number of oxidation states. Thus oxy-anions of phosphorus are very poor oxidising agents. On the other hand, except PO^{3-}_4, the oxy-anions are good reducing agents, the reducing action in basic solutions being stronger than in acid solutions.

Arsenic acid (H_3AsO_4) is obtained by heating arsenic trioxide, As_2O_3, or the metal with concentrated nitric acid. This is a tribasic acid and is weaker than phosphoric acid ($K = 5 \times 10^{-3}$). It liberates iodine from an iodide solution.

$$AsO_4^{3-} + 2 I^- + 4 H^+ \rightarrow AsO_2^- + I_2 + 2 H_2O$$
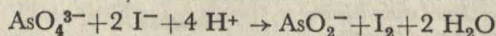
Arsenious acid (H_3AsO_3) is obtained by dissolving As_2O_3 in water. It is a very weak acid ($K = 5 \times 10^{-10}$). H_3AsO_3 is used as reducing agent. In basic solution, it is easier to oxidise arsenic to a higher oxidation state than in acidic solution. In acidic solution, AsO^{2-}_4 is a mild oxidising agent but in basic medium, it loses its oxidising power. Antimony does not form any acid. In acid solution, Sb_2O_3 or Sb_2O_5 dissolves to produce SbO^+ or $[Sb(OH)_2]^+$.

Bismuth exists in aqueous solution only in the $+3$ oxidation state. Bi_2O_3 dissolved in acids gives BiO^+ or $[Bi(OH)_2]^+$. The $+5$ oxidation state of bismuth can only be obtained by oxidising bismuth in basic medium with a powerful oxidising agent like Na_2O_2 or Cl_2, whereby it gives sodium bismuthate. It is not certain if sodium bismuthate is $NaBiO_3$ or a mixture of Na_2O and Bi_2O_5.

16.5.6 Halides

The elements of this group combine directly with halogens to form halides of the type MX_3. These halides are predominantly covalent and like NH_3, have a tetrahedral structure with one position occupied by a lone pair. Except NF_3, the nitrogen halides are unstable and decompose with explosive violence. Nitrogen trifluoride is stable, and inert. NF_3 should act as a Lewis base, since it has a pair of non-bonded electrons, but there are no known compounds in which it donates electrons to other reagents. Apparently, this lack of basic

properties is because of the high electronegativity of fluorine atoms. The fluorine atoms draw the electron density away from the nitrogen atom and make NF_3 a poor electron donor.

As the non-metallic character decreases from phosphorus to bismuth, there is an increase in the ionic properties of the halides. This is reflected in increase in their boiling points—PCl_3 (74°C), $AsCl_3$ (122°C), $SbCl_3$ (219°C), $BiCl_3$ (441°C)—and in their decreasing tendency towards hydrolysis. The hydrolysis of NCl_3 and PCl_3 is complete and that of $AsCl_3$ nearly so. Both $SbCl_3$ and $BiCl_3$, however, hydrolyse only partially giving the corresponding oxy-salts:

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$$
$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$
$$AsCl_3 + 3H_2O \rightarrow H_3AsO_3 + 3HCl$$
$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$$
$$BiCl_3 + H_2O \rightarrow BiOCl + 2HCl$$
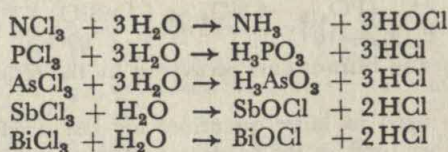
Nitrogen is unable to form pentahalides owing to the absence of suitable d orbitals, but the other elements do so by the promotion of an electron from the $3s$ to the $3d$ orbital. PF_5, PCl_5, PBr_5, SbF_5 and $SbCl_5$ are known. These molecules have a trigonal bipyramid shape in the gas phase (see Fig. 16.11).

The most important oxyhalides of phosphorus are POX_3 (phosphoryl halides; X=halide). These are prepared by the hydrolysis of PX_5 in a limited amount of water or by the reaction of trihalides with oxygen. Their structures are tetrahedral:

$$2PX_3 + O_2 \rightleftharpoons 2POX_3$$
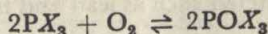
16.5.7 Nitrides
Nitrogen combines at high temperatures with many metals to form nitrides:

$$M + N \rightarrow MN$$
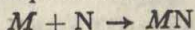
The nitrides, like carbides, are of three types: (i) ionic nitrides which are formed by alkaline earth metals, Li, Zn, Cd (which give ammonia on hydrolysis), (ii) interstitial nitrides formed by the union of nitrogen with transition metal ions (stoichiometry and structure are not fixed), and (iii) covalent nitrides formed by the elements of groups IIIA, IVA, and VA. Among covalent nitrides, boron nitride, BN, is a very interesting compound. Boron nitride is isoelectronic with carbon and it also exists in two forms: graphite-like and diamond-like. In the graphite-like form, there are planes consisting boron and nitrogen atoms bonded at a distance of 1·45 A in hexagonal rings; each plane is separated from the other by van der Waals forces. The distance between two planes is 3·34 A. Therefore, its properties are similar to graphite. Diamond-like boron nitride has a structure with alternate boron and nitrogen atoms instead of carbon atoms.

16.5.8 Sulphides
Tetranitrogen tetrasulphide, N_4S_4 is prepared by the action of NH_3 on S_2Cl_2 or SCl_2. It is a yellow crystalline solid.

$$6S_2Cl_2 + 16NH_3 \rightarrow N_4S_4 + 12NH_4Cl + 8S$$
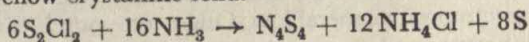
Other sulphides are prepared by the direct interaction of sulphur with elements at high temperatures. The sulphides of arsenic and antimony can also be prepared by the action of hydrogen sulphide on the appropriate metallic salts. Arsenic and antimony sulphides are dissolved in ammonium sulphide to give

thio-anions like $(AsS_3)^{3-}$, $(SbS_3)^{3-}$, $(AsS_4)^{3-}$, $(SbS_4)^{3-}$. Bismuth trisulphide is not soluble in ammonium sulphide. The structures of M_4S_6 and M_4S_{10} are similar to those of P_4O_6 and P_4O_{10}.

16.5.9 Occurrence and Preparation of the Elements

Nitrogen exists in free state in the atmosphere. In the bound form, it occurs as nitrates, ammonium compounds, organic compounds and so on. Phosphorus exists as calcium phosphate while arsenic, antimony and bismuth exist as oxides or sulphides. Phosphorus is obtained by the action of the phosphate with silica and coke at high temperatures:

$$2\,Ca_3(PO_4)_2 + 6\,SiO_2 \rightarrow 6\,CaSiO_3 + P_4O_{10}$$
$$P_4O_{10} + 10\,C \qquad \rightarrow P_4 + 10\,CO$$
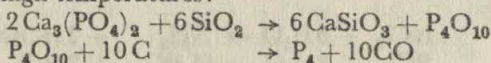
Arsenic, antimony and bismuth are recovered by the reduction of their oxides with carbon.

Nitrogen gas is used in large quantities for the production of ammonia. Smaller amounts are used in the hardening of steel and in reaction chambers where an inert atmosphere is desired.

Elemental phosphorus is used in the manufacture of certain widely used bronze alloys, in the production of phosphoric acid, H_3PO_4, and in the manufacture of matches, tracer bullets and pesticides.

Arsenic, antimony and bismuth are used mainly with metals to make alloys with certain desirable properties. A trace of arsenic is added to lead shot to increase the hardness and surface tension of lead. Antimony is used in alloys to dilute more expensive metals such as lead and tin. *Babbitt*, an alloy of antimony, is used in bearings.

Bismuth and antimony alloys tend to expand when they solidify. Hence, they are useful in making good castings.

16.6 GROUP VIA ELEMENTS: OXYGEN FAMILY

Group VIA of the periodic table consists of five elements—oxygen, sulphur, selenium, tellurium and polonium, the last one being radioactive. The first four elements are nonmetallic in character and are collectively called as *chalcogens* or ore-forming elements, because many metal ores are oxides or sulphides. Oxygen is highly electronegative and differs markedly from the other members. The next three elements sulphur, selenium and tellurium have many chemical properties in common.

16.6.1 General Characteristics

The electronic configurations and some physical properties of group VIA elements are listed in Table 16.11. These elements have six electrons (ns^2np^4) in their outermost energy levels, one electron less than the halogens and two electrons less than the noble gases, and hence they function as electron acceptors.

Tellurium and selenium form telluride (Te^{2-}) and selenide (Se^{2-}) ions respectively by accepting two electrons, but these exist as ions only in combination with strongly electropositive metal ions. Other compounds of these elements are nearly covalent compounds.

Group VIA elements also form compounds like $(CH_3)_2S$ in which there are two electron pair bonds; compounds like RS^- with one electron pair bond and one negative charge, and compounds like R_3S^+ with three electron pair bonds

and one positive charge. The inert gas configurations of the elements are also obtained by double bond formation in the case of oxygen and sulphur, e.g. $O=C=O$, $S=C=S$, etc.

The chemistry of oxygen is different from that of the other elements of this group. The other four elements differ in their properties gradually through the sequence S, Se, Te and Po. The reasons for oxygen to be different from other elements are: (*i*) large electronegativity of oxygen which results in predominantly ionic compounds; (*ii*) the availability of *d* orbitals in S, Se, Te and Po for bond formation and (*iii*) a much larger tendency of catenation in sulphur whereby it forms polysulphides, S^{2-}_n; sulphanes $H-S_n-H$; and polysulphonic acids, $HO_3S-S_n-SO_3H$.

After oxygen, the properties of the elements vary gradually from sulphur to polonium. Thus, the metallic character of the element increases, the thermal stability of the hydrides, H_2X, decreases, the tendency to form anionic complexes increases ($SeBr^{2-}_6$, $TeBr^{2-}_6$, PoI^{2-}_6) and the stability of the compounds in which the elements are present in high oxidation states ($+6$, $+4$) decreases. All these gradual changes are due to the gradual increase in atomic radii and decrease in electronegativities of the elements. The oxidation potentials show that the tendency to form A^{2-} (*aq*) (*A*=group VIA element) decreases rapidly with the increase in atomic number.

The large difference in the melting and boiling points between oxygen and sulphur can be attributed, in part, to the fact that, whereas oxygen exists in the form of O_2 molecules, sulphur forms S_8 molecules.

Table 16.11 Physical Properties of Group VIA Elements[1]

| Property | Element | | | |
	Oxygen	Sulphur	Selenium	Tellurium
Atomic mass	15·9994	32·064	78·96	127·60
Atomic number	8	16	34	52
Isotopes	16, 17, 18	32, 34, 33, 36	80, 78, 82, 76, 77, 74	130, 128, 126, 125, 124, 123, 122, 120
Electronic structure	$2s^2\,2p^4$	$3s^2\,3p^4$	$3d^{10}\,4s^2\,4p^4$	$4d^{10}\,5s^2\,5p^4$
Atomic radius, A	0·74	1·03	1·17	1·37
Ionic radius, A	1·40	1·84	1·98	2·21
Electronegativity	3·5	2·5	2·4	2·1
Ionisation energy, eV	I. 13·61	10·36	9·75	9·01
	II. 35·15	23·4	21·3	—
Density, g cc^{-1}	1·27 (solid)	2·06 (rhombic)	4·81 (grey)	6·25
Melting point, °C	−218·9	119 (monoclinic)	220·2 (grey)	450
Boiling point, °C	−182·9	444·6	684·8	1,390
Electrode potential, $E°$, V $A_2(g)+2\,e+(aq)\rightarrow 2A^-(aq)$[2]	+0·401	−0·48	−0·92	−1·14

[1]For symbols refer to Table 16.1

[2]*A*, any element of group VIA

Oxygen molecule has a high bond energy (118 kcal mol^{-1}) and would be expected to be less reactive compared to fluorine which has a bond energy of only 38 kcal mol^{-1}. This is in fact true. Relatively large activation energies are required to initiate most oxidation reactions involving oxygen molecules. However, many of these reactions are highly exothermic and, once initiated, proceed vigorously. With oxygen, positive oxidation state ($+2$) is found only in compounds of fluorine, since fluorine is the only element more electronegative than oxygen.

16.6.2 Allotropic Modifications

All the elements of the group exhibit allotropy. Oxygen exists in diatomic (O_2) and triatomic (O_3) states. Oxygen gas is diatomic with a substantial dissociation energy and is paramagnetic with two unpaired electrons (see Chapter 4 for discussion of O_2 and its ions). Ozone, O_3, which is formed by passing a silent electric discharge through oxygen and condensing the product at 77 K, is a powerful oxidising agent.

$$O_3 + 2H^+ + 2e \rightarrow O_2 + H_2O \qquad (E^\circ = 2 \cdot 07V)$$
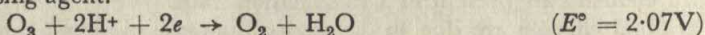
Ozone oxidises NO, ClO_2 and KI to form NO_2, Cl_2O_6 and I_2 respectively. The structure of ozone is given in Fig. 16.14. We see that the bond distance in ozone is exactly the same as that in the superoxide ion (1·28A). The resonance structures of ozone are also shown in Fig. 16.14.
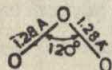
Fig. 16.14 Ozone and its resonance hybrids
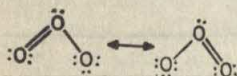
Sulphur exists in several allotropic forms. The comm⁀n form is the ortho-rhombic sulphur. It is bright yellow in colour, and insoluble in water, but soluble in carbon disulphide. Its density is 2·07 g cc^{-1}. When rhombic sulphur is heated above 95·5°C it slowly transforms to monoclinic sulphur, which is dull yellow and insoluble in water, but soluble in carbon disulphide.

(a)

Both the rhombic and monoclinic forms of sulphur are composed of S_8 molecules. The eight atoms in the molecule are linked together in a puckered ring (Fig. 16.15a). The plastic sulphur which is obtained by pouring liquid sulphur into water contains zig-zag long chains of sulphur atoms (Fig. 16.15b). It is insoluble in carbon disulphide. On standing, it is slowly converted to rhombic or monoclinic sulphur, depending on the temperature at which it is maintained.

(b)

Fig. 16.15 (a) Puckered rings of S_8 and (b) chains of sulphur (plastic sulphur)

Sulphur molecules containing S_8 become less stable as the temperature is raised. The rings are ruptured and long chains of sulphur atoms formed by the homolytic fission of S–S bonds in the S_8 rings. The existence of these sulphur chains explains a peculiar property of

liquid sulphur. The viscosity of sulphur increases as the temperature is raised from 114·5° to about 200°C; after this, it decreases gradually till the boiling point (444·6°C) is reached. When sulphur first melts, it can be poured easily, but at about 200°C it has the consistency of thick tar. Sulphur molecules still exist as S_8 rings just above the melting point, and these rings slip and roll over one another easily thus lowering viscosity. But when liquid sulphur is heated, the rings are broken into chains. These chains are free radicals and they in turn attack other rings and chains so that at any temperature an equilibrium between rings and chains of various length exists. At 200°C these chains reach their maximum length. These long molecules become entangled with one another making sulphur very viscous. Above 200°C, these chains break up further and sulphur acts like a typical liquid.

At temperatures above the boiling point, sulphur forms a red vapour, which turns to yellow as the temperature is raised. The vapour is believed to consist of a mixture of S_8, S_6 and S_2 molecules. At 1000°C, the vapour consists primarily of S_2 molecules. This species is paramagnetic and has a structure similar to that of O_2.

Selenium has three important allotropes, namely, rhombic, monoclinic and grey forms. The rhombic variety consists of Se_8 molecules, the atoms being arranged in an open ring. The monoclinic form which also consists of Se_8 molecules exists in the form of puckered rings similar to those of S_8 molecules. The grey form which is most stable, consists of regularly arranged spirals of selenium atoms. Several allotropes of tellurium are described and the common variety is isomorphous with grey selenium.

16.6.3 Trends in Chemical Properties

Sulphur can act either as an oxidising agent or as a reducing agent. It combines with all the elements except the platinium metals, gold and the noble gases. Yet, sulphur is not very reactive unless heated above its melting point. Selenium and tellurium have similar chemical properties but are somewhat less reactive than sulphur: $Fe + A \rightarrow FeA$, where $A = S$, Se, or Te. Sulphur reacts more energetically than selenium and tellurium, and less energetically than oxygen. The heat evolved when a powdered metal is oxidised by powdered sulphur is often large enough to make the products red hot. Some metals like copper, silver and mercury show a greater chemical affinity for sulphur than for oxygen. This is because a stronger bond is formed when the larger sulphide ion is polarised by these small positive metal ions.

The elements, S, Se and Te when burnt in air form dioxides with the general formula AO_2. Sulphur dioxide can also be prepared by the action of acid on sulphites, metabisulphites and thiosulphates. Selenium dioxide and tellurium dioxide are prepared by acidifying selenities and tellurities respectively. Heating of selenious and tellurous acids produces SeO_2 and TeO_2 respectively.

Sulphur dioxide is a gas (b.p. -110°C) and forms discrete molecules even in the solid state whereas the other oxides are solids. All the oxides are acidic in nature. Their acidic nature and stability decrease with increase in atomic number of the elements. The reaction of the dioxides with water also differs. Sulphur dioxide dissolves in water but the acid H_2SO_3 (sulphurous), cannot be isolated. Sulphur dioxide is a poor reducing agent in acid and neutral solutions, but in basic solution it is a powerful reducing agent. Thus, ferric salts, iodine, and permanganate (Mn^{4+}) are reduced to ferrous, iodide, and Mn^{2+} respectively.

Sulphur dioxide is an angular molecule with an O—S—O angle of 119°. In this oxide, sulphur is sp^2 hybridised and the S—O bond length is 1.43A suggesting a double bond character. In this molecule, besides $p\pi$—$p\pi$ bonding

there is some $p\pi$—$d\pi$ bonding (Fig. 16.16) due to the overlap of the $p\pi$ orbitals of oxygen with the vacant $d\pi$ orbital of sulphur. Selenium dioxide has a zig-zag chain structure (Fig. 16.17).

Oxygen
p π - orbital

Sulphur
dπ-orbital

(a)   (b)
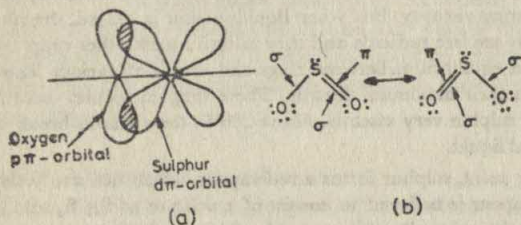
Fig. 16.16 (a) p-π, d-π overlap in SO_2 and (b) resonance structures in SO_2
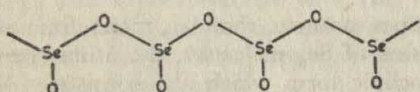
Fig. 16.17 Selenium dioxide chain

All the members of the group except oxygen, form trioxides, AO_3, with marked acidic properties. The conversion of SO_2 to SO_3 is favoured thermo-dynamically ($\Delta G° = -16\cdot7$ kcal mol^{-1}), but due to very high activation energy the rate of this reaction is very slow. The reaction is catalysed by vanadium pentoxide or platinised asbestos, and is used in the contact process for the manufacture of sulphuric acid. These trioxides give rise to higher oxy-acids, H_2AO_4, and series of isomorphous salts of the type M_2AO_4 (where $M =$ monovalent metal, $A =$ element of group VIA). The acid H_2AO_4 becomes much less acidic and more unstable as the atomic number of A increases. Thus, telluric acid is a very feeble acid and decomposes on warming.
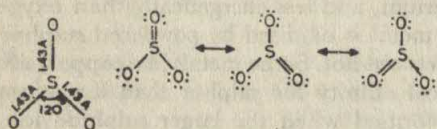
Fig. 16.18 Sulphur trioxide

In the gas phase, SO_3 is a planar triangular molecule with three equivalent S—O bonds (Fig.16.18). The bonding can be represented by the three resonance structures in Fig. 16.18.

Example 16.8 Write equations for the reactions of sulphur with (i) $S^{2-}(aq)$, (ii) $SO^{2-}_3(aq)$, (iii) Fe, (iv) F_2, (v) Cl_2, and (vi) HNO_3.

(i) $4S + S^{2-} \rightarrow S^{2-}_5$
    (pentasulphide)

(ii) $S + SO^{2-}_3 \rightarrow S_2O^{2-}_3$
    (thiosulphate)

(iii) $S + Fe \rightarrow FeS \xrightarrow{\text{sulphur}} FeS_2$

(iv) $S + F_2 \rightarrow SF_4$

(v) $2S + Cl_2 \rightarrow S_2Cl_2 \xrightarrow{\text{excess } Cl_2} SCl_2 \xrightarrow{\text{liq. } Cl_2} SCl_4$
    (sulphur   (sulphur di-   (sulphur tetra-
    monochloride)   chloride)   chloride)

(vi) $S + 6\ HNO_3 \rightarrow H_2SO_4 + 2\ H_2O + 6\ NO_2$
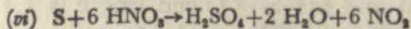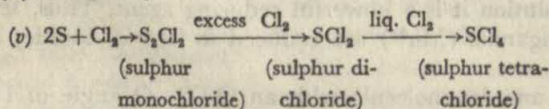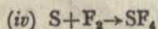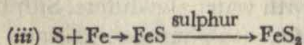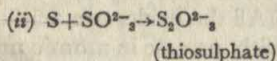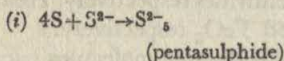
16.6.4 Oxides

A considerable amount of energy is needed to form O^{2-} from molecular oxygen:

$$\frac{1}{2}O_2(g) \rightarrow O(g) \quad \Delta H = 60 \text{ kcal mol}^{-1}$$

$$O(g) + 2e \rightarrow O^{2-}(g) \quad \Delta H = 176 \text{ kcal mol}^{-1}$$

$$\frac{1}{2}O_2(g) + 2e \rightarrow O^{2-}(g) \quad \Delta H = 236 \text{ kcal mol}^{-1}$$
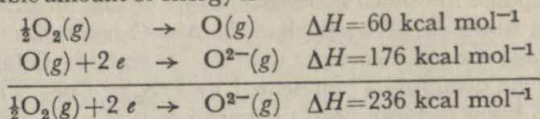
In spite of this large amount of energy required to form O^{2-}, many ionic oxides exist because the lattice energies (containing the small ion O^{2-} with O—O distance 1.4A) are very high. In some cases, the lattice energy is large enough to allow the formation of the metals in unusually high oxidation states. In some instances, the lattice energy is not sufficient to permit the complete ionisation of the metal ions and the bonds between metals and oxygen possess substantial covalent character. Many non-metals form molecular covalent compounds, such as CO_2 and P_4O_6.

We can classify oxides into four classes.

Basic oxides: These have discrete O^{2-} in the solid state. In aqueous solution these ions get hydrolysed.

$$O^-_2 + H_2O \rightleftharpoons 2OH^-(aq) \qquad (K > 10^{22})$$
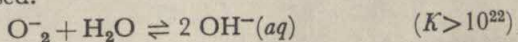
with acids, they form salts:

$$M^{2+}O^{2-} + 2HX \rightarrow MX_2 + H_2O$$
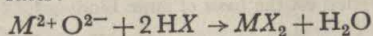
Acidic oxides: These are the covalent oxides of non-metals. These give acids with water.

$$SO_2 + H_2O \rightarrow H_2SO_3$$
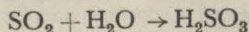
Basic and acidic oxides combine together to give salts:

$$Na_2O + SiO_2 \rightarrow Na_2SiO_3$$
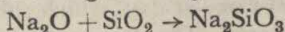
Amphoteric oxides: These oxides are formed by elements with less metallic character. These behave like acids towards bases and as bases towards acids:

$$ZnO + 2H_3O^+ \rightarrow Zn^{2+} + 3H_2O$$

$$ZnO + 2OH^- + H_2O \rightarrow [Zn(OH)_4]^{2-}$$
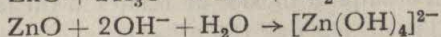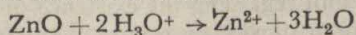
Non-stoichiometric oxides: These are formed mostly by transition metals and some lanthanides (rare earths). (See Chapters 7 and 17.)

16.6.5 Chalcogenides

Metals when heated with sulphur, selenium and tellurium form sulphides, selenides, and tellurides respectively. These are binary compounds having rather complex structures. Elements of groups IA and IIA form ionic sulphides. They dissolve in water giving S^{2-} which are extensively hydrolysed producing hydrogen sulphide.

$$S^{2-} + 2H_2O \rightarrow H_2S + 2OH^-$$
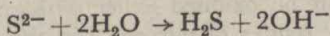
Most metallic sulphides cannot be classified as ionic sulphides. They generally exhibit variable stoichiometry (and are often non-stoichiometric compounds, e.g. FeS, CrS).

In general, the metal-sulphur bond has more covalent character than the M—O bond. This is because sulphur is much less electronegative than oxygen.

Besides the double and triply charged metal ions (which have relatively small sizes) polarise a sulphide ion much more than an oxide ion, imparting a larger degree of covalency to the M—S bond (than the M—O bond). Similarly, M—Se and M—Te bonds are more covalent than M—S and M—O bonds.

Another class is the disulphides represented by FeS_2 or CoS_2. They contain S_2 units with S—S bond distance nearly equal to that of a S—S single bond. The disulphides assume either the pyrite or the distorted sodium chloride structure. In FeS_2 which has the NaCl structure the iron atoms occupy Na^+ sites and the disulphides occupy Cl^- sites.

One of the most important properties of sulphur is *catenation* which is responsible for the formation of polysulphides containing $(S_n)^{2-}$ ions. In these type of sulphides, the value of n ranges from two to six. The polysulphides contain chains of sulphur atoms bonded to one another. On acidification, they form sulphanes having the general formula, H_2S_n $(2<n<6)$. Polysulphides are prepared by dissolving sulphur in a hot concentrated solution of alkali. In the formation of polysulphides, the S_8 rings are broken by S^{2-} which functions as a Lewis base. The S_8 ring can be broken at various places giving chains of different lengths.

Example 16.9 Why are the measured values of the lattice energies of transition metal sulphides higher than the values predicted on the basis of ionic binding?

The doubly and triply charged transition metal ions are relatively small and greatly distort the large sulphide ions. Therefore, there is a large amount of covalent bonding between the sulphide and metal ions, and hence the larger values of lattice energies.

16.6.6 Oxy-acids

Sulphur forms a number of oxy-acids of which sulphurous and sulphuric acids are the most important ones. The aqueous solution of sulphurous acid is formed by dissolving sulphur dioxide in water. It does not exist in the free state; even in aqueous solution, there is no evidence that H_2SO_3 molecules exist, but there is no doubt regarding the existence of SO_3^{2-} and HSO^-_3. An aqueous solution of sulphur dioxide dissociates in the following manner:

$$SO_2(aq) + H_2O \rightleftharpoons HSO_3^- + H^+ \qquad K = 1\cdot3 \times 10^{-2}$$
$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \qquad K = 5\cdot6 \times 10^{-8}$$
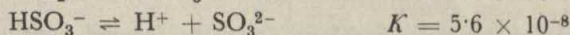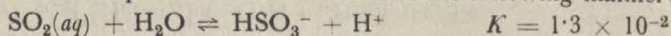
The sulphite ion can react with elemental sulphur to form thiosulphate ions $S_2O_3^{2-}$. In acid solution, the $S_2O_3^{2-}$ decomposes to give sulphite ions and sulphur.

$$S + SO_3^{2-} \longrightarrow S_2O_3^{2-}$$
$$S_2O_3^{2-} \xrightarrow{\text{acid}} S + SO_3^{2-}$$
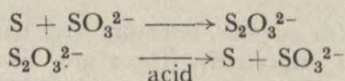
An aqueous solution of sulphur dioxide acts as a mild reducing agent and is often used as a bleaching agent.

Sulphur dioxide can be oxidised either with oxygen (in the presence of platinised asbestos) or oxides of nitrogen (by the intermediate formation of nitrosyl sulphuric acid, $OHSO_2ONO$), to produce sulphur trioxide which when dissolved in water gives sulphuric acid. Hydration of sulphur trioxide takes place in two steps.

$$2SO_3(g) + H_2O \rightarrow H_2S_2O_7(l)$$
$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$
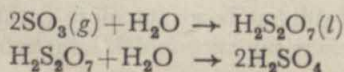
Pure sulphuric acid is a highly viscous liquid and is a good conductor of electricity due to the following equilibrium:

$$2H_2SO_4 \rightleftharpoons (H_3SO_4)^+ + HSO_3^-$$
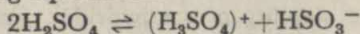
H_2SO_4 forms several hydrates on combination with water. Its affinity for water is so large that it removes elements of water from several compounds and is used as a dehydrating agent.

$$\begin{align} C_{12}H_{22}O_{11} + H_2SO_4 &\rightarrow 12C + 11H_2O + H_2SO_4 \\ \text{(Sugar)} & \\ HCOOH + H_2SO_4 &\rightarrow CO + H_2O + H_2SO_4 \\ CuSO_4 \cdot 5H_2O + H_2SO_4 &\rightarrow CuSO_4 + 5H_2O + H_2SO_4 \end{align}$$
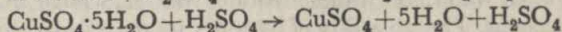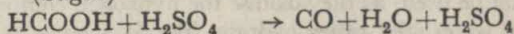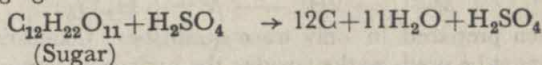
Hot concentrated sulphuric acid acts as an oxidising agent, since it oxidises copper, carbon, sulphur and iodide ions.

$$\begin{align} Cu + 5H_2SO_4 &\rightarrow Cu^{2+} + SO_2 + 4HSO^-_4 + 2H_3O^+ \\ C + 2H_2SO_4 &\rightarrow CO_2 + 2H_2O + 2SO_2 \end{align}$$
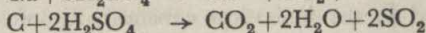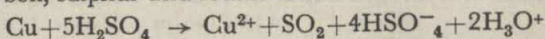
On electrolysis, sulphuric acid yields peroxy-di-sulphuric acid ($H_2S_2O_8$) which is a powerful oxidising agent.

$$S_2O_8^{2-} + 4H^+ + 2e \rightarrow 2H_2SO_4 \qquad E° = 2 \cdot 01 \text{ V}$$
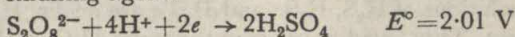
Sulphuric acid reacts with phosphorus pentachloride producing chlorosulphonic acid and sulphuryl chloride:

$$\begin{align} PCl_5 + SO_2(OH)_2 &\rightarrow POCl_3 + HCl + Cl \cdot SO_2 \cdot OH \\ PCl_5 + Cl \cdot SO_2 \cdot OH &\rightarrow POCl_3 + HCl + Cl \cdot SO_2 \cdot Cl \end{align}$$
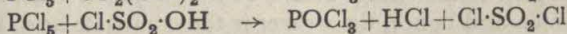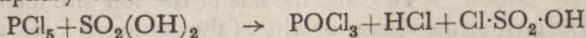
Chlorosulphonic acid and sulphuryl chloride are hydrolysed by water to give sulphuric acid. This suggests that the two OH groups in H_2SO_4 are attached to the SO_2 moiety. Thus, the formula of H_2SO_4 can be written as $SO_2 \cdot (OH)_2$. Sulphur is *sp³* hybridised in sulphuric acid and its structure is represented below.

Selenium forms selenous and selenic acids and tellurium forms tellurites and telluric acid. Selenous acid is formed by dissolving SeO_2 in water. TeO_2 is not soluble and therefore H_2TeO_3 has not been isolated, but tellurites are known. On oxidation, selenites and tellurites form selenic acid (H_2SeO_4) and telluric acid, $Te(OH)_6$. In the weak telluric acid, tellurium ion is linked with six OH groups at the corners of an octahedron.

Sulphurous acid, H_2SO_3 gives sulphites. Seleneous acid gives selenites and tellurous acid, tellurites. Likewise one gets from H_2SO_4 sulphates; H_2SeO_4, selenates; and H_2TeO_4, tellurates. Since H_2SO_4, H_2SeO_4 and H_2TeO_4 are diprotic acids, there are normal salts like K_2SO_4 and K_2SeO_4 and also acid salts like, $RbHSO_4$ and $RbHTeO_4$. Selenates are similar to sulphates and contain the same amount of water of crystallisation and form isomorphous double salts and alums. All these elements form compounds of the type MO_2Cl_2 which are readily hydrolysed by water.
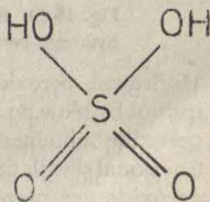
Example 16.10 Suggest a possible explanation why H_6TeO_6 exists while H_6SO_6 does not.

Tellurium is a much larger atom than sulphur and it can accommodate six oxygen atoms around it while sulphur cannot. Therefore, tellurium forms H_6TeO_6 while sulphur does not form a similar compound.

16.6.7 Hydrides

All these elements form stable volatile bivalent hydrides, H_2O, H_2S, H_2Se, H_2Te, and H_2Po. The stability of the hydrides decreases gradually from H_2O to H_2Po. Hydrogen sulphide, hydrogen selenide and hydrogen telluride, are prepared by the action of dilute hydrochloric acid on metal sulphides, selenides, and tellurides respectively.

$$MX(s) + 2H^+ \longrightarrow M^{2+} + H_2X(g)$$
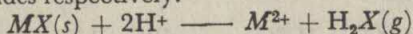
H_2Po has been prepared in only trace quantities. Oxidising acids such as nitric acid cannot be used, as they oxidise the hydrogen compounds to the free element. Unlike water, the other hydrides like H_2S have unpleasant odours and are poisonous. The volatility of hydrides increases markedly from H_2O to H_2S and then decreases. The relatively low volatility of water is due to its association by means of hydrogen bonds both in solid and liquid states (see Chapter 8).

Let us examine the trend in the ionisation constant, K_i, of the aqueous solutions of the hydrides. The small value of K_i for H_2S indicates that the small sulphur atom holds on to hydrogen more tightly than the larger tellurium atom does. The water solutions of H_2S, H_2Se and H_2Te are acidic, H_2Te being the strongest of the three. Thus, acidity varies in the series $H_2O < H_2S < H_2Se < H_2Te$. The charge densities of the conjugate bases of these oxides vary in the order, $O^{2-} > S^{2-} > Se^{2-} > Te^{2-}$ and the size of the ion also increases in the same order. The greater the charge density of the conjugate base, greater is its affinity for a proton and hence, the weaker is the conjugate acid. Further, the larger ions would have greater stability since the charge can be distributed over a larger volume. Therefore, H_2O is the weakest acid among the hydrides because the oxide ion attracts a proton more effectively.

Another important hydride of oxygen is hydrogen peroxide, H_2O_2 (Fig. 16.19). It is prepared by treating any metal peroxide (BaO_2 or Na_2O_2) with dilute sulphuric acid. Industrially, hydrogen peroxide is prepared by the electrolysis of concentrated sulphuric acid or of concentrated solution of ammonium sulphate. The following anodic oxidation reaction occurs.
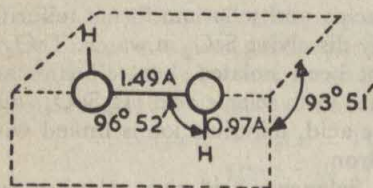
Fig. 16.19 Structure of hydrogen peroxide

$$2HSO_4^- \rightleftharpoons S_2O^{2-}_8 + 2H^+ + 2e^-$$
$$2H_2O + S_2O^{2-}_8 \rightarrow H_2O_2 + 2HSO_4^-$$
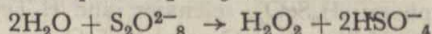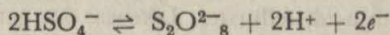
Hydrogen peroxide can also be manufactured by autoxidation of anthraquinol by blowing air through its solution in benzene. The solution of hydrogen peroxide obtained from these reactions is dilute and it is concentrated by fractional distillation under reduced pressure at 60°C. Pure crystals of hydrogen peroxide are prepared by fractional crystallisation of 90 per cent hydrogen peroxide.

Hydrogen peroxide is a bluish viscous liquid, and is associated through hydrogen bonding. It has a higher dissociation constant than water.

$$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + (OOH)^- \quad (K = 1 \cdot 5 \times 10^{-2})$$
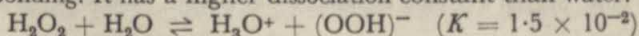
It has a strong tendency to decompose to yield oxygen. This forms the basis of

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (\Delta H = -47 \text{ kcal mol}^{-1})$$
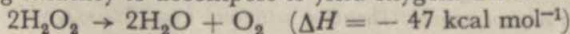
its bleaching action. The strength of hydrogen peroxide is designated in terms

of the volume of oxygen produced at STP. For example, 1 ml of 20 volume H_2O_2 solution produces 20 ml of oxygen at STP on decomposition. Hydrogen peroxide acts both as an oxidising and as reducing agent, as the following schemes show:

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \qquad (E° = + 1·77 \text{ V})$$
$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e \qquad (E° = + 0·66 \text{ V})$$
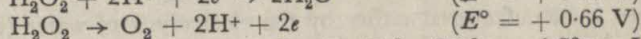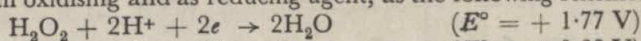
Consequently, hydrogen peroxide oxidises I^-, Fe^{2+}, SO^{2-}_3 and S^{2-} to I_2, Fe^{3+}, SO^{2-}_4 and S respectively. It reduces ammoniacal $AgNO_3$, $KMnO_4$, $HClO$ and O_3 to Ag, Mn^{2+}, Cl^- and O_2 respectively.

Example 16.11 Calculate the normality of 30 volume H_2O_2 solution.

According to the equation, $2 H_2O_2 \rightarrow 2 H_2O + O_2$, 68g of H_2O_2 produce 22·4 litre of O_2 at STP
Now, 30 volume H_2O_2 means that

1 ml H_2O_2 gives 30 ml of O_2 at STP

or   1 litre H_2O_2 gives 30 litre of O_2 at STP

So   1 litre of H_2O_2 contains

$$\frac{30 \text{ litres}}{22·4 \text{ litre}} \times 68 = 91·2 \text{ g of } H_2O_2$$

Hence the normality of hydrogen peroxide solution

$$\frac{\text{CONCENTRATION}}{\text{EQUIVALENT MASS}} = \frac{91·2}{17} = 5·37 \text{ N}$$

16.6.8 Halides

The known fluorides of sulphur are the tetrafluoride, SF_4, the hexafluoride, SF_6 and the disulphur decafluoride, S_2F_{10}. Direct fluorination of sulphur yields SF_6 as the principal product along with some S_2F_{10}. Sulphur tetrafluoride is obtained by the reaction of sulphur chloride with sodium fluoride in a polar solvent at 70–90°C. The tetrafluoride is highly reactive, and is hydrolysed rapidly to SO_2 and HF.

$$SF_4 + 2H_2O \rightarrow SO_2 + 4HF$$
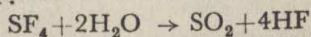
Sulphur tetrafluoride has a trigonal bipyramidal structure with one of the equatorial positions occupied by an unshared pair of electrons. Sulphur hexafluoride is extremely inert (see Chapter 4 for structure). It can be made to react with other substances only at temperatures above 350°C. Selenium and tellurium tetrafluorides are also highly reactive. Hexafluorides of selenium and tellurium are more reactive than that of sulphur because of the larger sizes of their atoms.

The chlorides, S_2Cl_2, SCl_2, SCl_4, Se_2Cl_2, $SeCl_2$, $SeCl_4$, $TeCl_2$ and $TeCl_4$ have been prepared, as have been the bromides. The only iodide stable at room temperature is TeI_4. As the halogen atom becomes larger, the maximum coordination number of the group VIA element becomes smaller. Thus, there are no known hexachlorides, no tetrabromides, and only one stable iodide.

16.6.9 Abundance, Extraction and Uses of Group VIA Elements

Oxygen, the most abundant of all elements, exists in free form and makes up 20·9 per cent by volume of the atmosphere. In the form of ores, it makes up 46·6 per cent of the earth's crust and as water it comprises 89 per cent of the oceans. Sulphur occurs in minerals either in an oxidised state as sulphates or in the reduced state as sulphides. *Gypsum*, $CaSO_4·2H_2O$ (with low solubility in water) and *epsom salt*, $MgSO_4·7H_2O$ (with high solubility in water) are the

two common sulphate minerals. *Galena* PbS, *iron pyrites* FeS, and *zinc blende* ZnS, are important sulphide minerals. Sulphur occurs in a free state in large underground deposits. The other elements of group VIA scarcely occur in nature.

Oxygen is manufactured either by the electrolysis of water (containing a trace of sulphuric acid) or by the fractional distillation of liquid air. It is prepared in the laboratory by the thermal decomposition of oxidising agents such as $KClO_3$ (with MnO_2 as catalyst), $KMnO_4$, PbO_2, HgO, H_2O_2 or nitrates. Abundant deposits of sulphur are found in Italy and in the United States of America. Sulphur is pumped out of natural underground deposits by first melting it there with superheated water at 170°C and then forcing out the molten sulphur by pumping air at high pressure. It is also obtained as a by-product in the production of coal-gas, and sulphur dioxide is obtained as a by-product in the extraction of metals from sulphide ores.

Selenium and tellurium occur among sulphide ores and are obtained in concentrated form from anode sludge after the electrolytic refining of copper, and from flue dust produced during the roasting of ferrous sulphide.

Much of the sulphur produced is used for the manufacture of sulphuric acid. Smaller quantities are used in the preparation of other sulphur compounds, in the vulcanisation of rubber, and as a component in gunpowder and in insecticides.

Small quantities of selenium are used in the manufacture of ruby-red glass for signal lights and in ordinary glass to neutralise the green colour due to the presence of iron (II) silicate. Selenium is a poor conductor of electricity, but is a photoconductor (conducts in proportion to the intensity of light falling on its surface); this property is made use of in making light (exposure) meters used in photography. Selenium is also used in solar batteries.

16.7 GROUP VIIA ELEMENTS: HALOGEN FAMILY

The elements fluorine, chlorine, bromine, iodine and astatine are members of the *halogen group*. The name 'halogen' is derived from the Greek words meaning 'salt producing' on account of the fact that these elements are found in the salts present in sea-water.

16.7.1 General Characteristics

Halogens appear in the column just before the noble gases. The electronic configurations of these elements are ns^2np^5 which differ from the noble gas configuration by one electron (Table 16.12).

Because of their high electronegativity, halogens show practically no metallic properties, though solid iodine has a somewhat metallic appearance. Astatine, the heaviest member of the group may have some metallic properties, but it is a short-lived radioactive element. Halogens attain the noble gas configuration either by gaining one electron to form an univalent anion (as in LiF or NaCl) or by sharing to form a single covalent bond (as in CCl_4 or BF_3).

Halogens exist in the elemental form as diatomic molecules. Although the bond between the halogen atoms is fairly strong, the attraction between diatomic molecules due to van der Waals forces is quite weak. Since the strength of van der Waals forces is influenced by the number of electrons present in the molecule, this increases as we go down the group of halogens. Consequently,

Table 16.12 Physical Properties of Group VIIA Elements

Property	Element			
	Fluorine	*Chlorine*	*Bromine*	*Iodine*
Atomic mass	18·9984	35·453	79·909	126·9044
Atomic number	9	17	35	53
Isotopes	19	35, 37	79,81	127
Electronic structure	$1s^2 2s^2 2p^5$	$2p^6 3s^2 3p^5$	$3p^6 3d^{10} 4s^2 4p^5$	$4p^6 4d^{10} 5s^2 5p^5$
Atomic radius, A	0·72	0·99	1·14	1·33
Ionic radius, X^-, A	1·36	1·81	1·95	2·16
Electronegativity (Pauling scale)	4·0	3·0	2·8	2·5
Ionisation energy, eV	17·4	13·01	11·80	10·44
Density of liquid, g cc^{-1}	1·1	1·5	3·2	4·9 (solid)
Melting point, °C	−223	−102	−7·3	114
Boiling point, °C	−187	−34·3	58·8	183
Standard electrode reduction potential, V	2·85	1·36	1·065 (Br(1))	0·535 (I(s))
Heat of vapourisation, kcal mol^{-1}	1·64	4·42	7·42	10·38
Heat of dissociation, kcal mol^{-1} $X_2(g) \rightarrow 2X$	38	50	45·5	35·6
Colour and physical state	Pale yellow gas	Greenish yellow gas	Red liquid	Black solid (violet vapour)

at room temperature fluorine and chlorine are gases, bromine is a liquid while iodine is a solid. This trend can be verified by the heat of sublimation which progressively increases from fluorine to iodine.

The relative sizes of the halogen atoms, which depend on the electronic configuration, are particularly useful in correlating many of the physical and chemical properties, and also the sharp differences in properties between fluorine and other halogens.

The ionisation energies of halogens are very high, indicating little tendency on their part to lose electrons. The ionisation energy of fluorine is highest because electrons are firmly held in the small fluorine atom and more energy is required to remove an electron from it. The ionisation energy of iodine is lowest.

The electron affinity (*EA*) of fluorine is 83 kcal mol^{-1}. The *EA*'s of chlorine and bromine are 88 and 82 kcal mol^{-1} respectively. Thus, halogens act as oxidising agents. The strength of an oxidising agent (oxidation potential) depends on several energy terms and is best represented by a Born-Haber type of cycle (see Chapters 7, 9 and 12).

$$\tfrac{1}{2}X_2(s) \xrightarrow{\Delta H(fusion)} \tfrac{1}{2}X_2(l) \xrightarrow{\Delta H(vap)} \tfrac{1}{2}X_2(g) \xrightarrow{\Delta H(dis)} X(g)$$

Oxidation Potential

$$X^-(\text{hydrated}) \xleftarrow{\Delta H(hyd)} X^-(g)$$
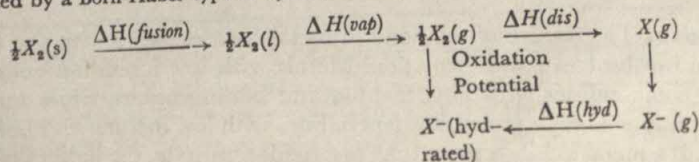
For fluorine and chlorine, which are gaseous at room temperature, the heats of fusion and evaporation are omitted and their oxidation potential depends only on the sum of the heat of dis-

sociation, electron affinity, and heat of hydration. Thus, despite the electron affinity of chlorine being highest, fluorine is the strongest oxidising agent. This is because of its low heat of dissociation and high heat of hydration (Table 16.13).

Table 16.13 Thermodynamic Data for the Halogens (kcal mol^{-1})

Halogen	$\frac{1}{2}$ (heat of fusion)	$\frac{1}{2}$ (heat of sublimation)	$\frac{1}{2}$ (heat of dissociation)	Electron affinity	Heat of hydration	Sum
F$_2$	—	—	+19	−83·5	−122	−186·5
Cl$_2$	—	—	+29	−87.3	− 89	−147·4
Br$_2$	—	+3·7	+23	−82·0	− 81	−136·4
I$_2$	+1·8	+5·2	+18	−75·6	− 72	−122·6

Fluorine oxidises any of the other halide ions in solution phase or even in dry state. Chlorine is the second best oxidising agent of the group and oxidises bromide and iodide ions, but not the fluoride ion. Bromine is an oxidising agent like chlorine, although not as powerful, it oxidises iodide ion, but not chloride ion. Iodine is a weaker oxidising agent than either bromine or chlorine. It does not oxidise either bromide or chloride ion. In general, any halogen of low atomic number will oxidise halide ions of higher atomic number.

$$F_2 + 2X^- \rightarrow 2F^- + X_2 \quad (X = Cl, Br, I)$$
$$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2 \quad (X = Br, I)$$
$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$
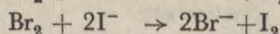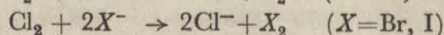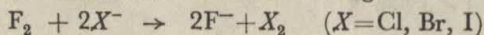
Fluorine atoms have no d orbitals which can be used for the bond formation. Fluorine cannot, therefore, have coordination number more than four or higher oxidation states in its compounds. Being the most electronegative element, it has always an oxidation number of -1. Other halogens show positive oxidation states with more electronegative elements. Most of these compounds contain oxygen which has electronegativity between that of fluorine and chlorine. The common oxidation numbers of halogens are -1, $+1$, $+3$, $+5$ and $+7$. Oxidation states of $+4$ and $+6$ are less common and occur in oxides and oxy-acids. Typical examples of compounds with different oxidation states of chloroine are: -1, HCl; $+1$, HOCl; $+3$, HClO$_2$; $+5$, HClO$_3$; and $+7$, HClO$_4$.

16.7.2 Halides

Halogens are very reactive elements. They combine directly with metals and non-metals to form the corresponding halides. The preparation and general properties of several halides were described in the other sections of this chapter. The general characteristics of halides are given below.

Metal halides: The nature of the bond in metal halides varies with the type of metal ion involved in bond formation. Metals with low ionisation energies form highly ionic halides with high melting and boiling points, while metals with high ionisation energies form covalent halides with low melting and boiling compounds. If a metal exhibits more than one oxidation state, the halides of the metal in the highest oxidation state will generally be the most covalent. Thus, SnCl$_4$ (b.p. $-33°$C) is more covalent than SnCl$_2$ (b.p. 246°C). Similarly, PbCl$_4$ and SbCl$_5$ are more covalent than PbCl$_2$ and SbCl$_3$ respectively.

Fluorine (being the most electronegative) has the highest ionic character among metal-halogen bonds. The ionic character of the M—X bond decreases in their order M—$F > M$—$Cl > M$—$Br > M$—I. Thus, AlF_3 is ionic while AlI_3 is essentially covalent; the crystals of the latter consist of the dimer Al_2I_6.

Most metal halides are soluble in water, the solubility increasing as we go from the fluoride to the iodide. For example, CaF_2 is only sparingly soluble in water, due to the fact that its ionic lattice energy is very high.

Halides of non-metals: With a given element, fluorine forms bonds that are substantially stronger than those formed by chlorine; the bonds with chlorine are stronger than those formed by bromine and iodine. As a result of the small dissociation energy of fluorine and the strong bonds it forms with non-metals, fluorides are generally the most stable of the non-metallic halides. Even though chlorine has the largest dissociation energy among the halogens, the bonds it forms with other elements are strong enough to make the non-metallic chlorides second only to the fluorides in stability. Despite the small bond energy of iodine molecule, iodides are generally the least stable of the halides because iodine forms only very weak bonds with the non-metals.

Hydrogen halides: Halogens combine with hydrogen to give hydrogen halides, but their affinity for hydrogen decreases from fluorine to iodine. Fluorine combines with hydrogen even in cold and dark, chlorine combines in sun light, bromine does so only on heating, iodine combines only when heated in the presence of a catalyst.

Hydrogen halides can be prepared by the action of water on phosphorous trihalides. Hydrogen chloride and hydrogen fluoride are prepared by treating soluble metallic chlorides and fluorides (NaCl or NaF) respectively with concentrated sulphuric acid. Hydrogen bromide and hydrogen iodide cannot, however, be prepared by this method because concentrated sulphuric acid will oxidise the bromide and iodide anions to free halogens.

A convenient method to obtain hydrogen iodide is to treat a suspension of iodine in water with hydrogen sulphide gas whereby iodine oxidises the sulphide ion to sulphur and hydrogen iodide is liberated.

$$H_2S + I_2 \rightarrow S + 2HI$$
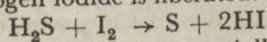
In the gas phase, hydrogen halides are essentially covalent diatomic molecules with their thermal stability decreasing with increasing atomic mass. Some of the properties of hydrogen halides are shown in Table 16.14. The anomalous behaviour of hydrogen fluoride compared to the other halides arises from the fact that hydrogen fluoride is a highly associated species with a high degree

Table 16.14 Some Properties of Hydrogen Halides

Property	Acid			
	HF	HCl	HBr	HI
Melting point, °C	−83	−114·8	−87	−50·7
Boiling point, °C	19·5	− 85	−66·8	−35·4
Bond Energy, kcal mol^{-1}	135	103	86	71
$\Delta G_f°$, kcal	65	23	13	6·2
Ionisation constant in H_2O	7×10^{-4}	10^7	10^9	10^{11}

of hydrogen bonding. This is reflected in its melting and boiling points, and also in its ionisation constant. The amount of ionic character in the H—X bond is also seen to follow the expected trend. In aqueous solution, hydrogen halides with the exception of HF ionise and function as strong acids. In aqueous solution, hydrogen fluoride is partially ionised whereas the other halides are completely ionised. Hydrofluoric acid is the weakest acid among them, its ionisation constant being only 7×10^{-4}. This weakly acidic nature of hydrofluoric acid is largely due to the strong H—F bond which reduces the tendency of the molecule to split up into ions in aqueous solution.

16.7.3 Halogen Oxides

Halogens combine with oxygen and form various oxides in which the oxidation state of the halogen atom varies from $+1$ to $+7$ (Table 16.15).

Table 16.15   Halogen Oxides

Oxidation state	Fluorine	Chlorine	Bromine	Iodine
$+1$	F_2O	Cl_2O	Br_2O	—
$+2$	F_2O_2	—	—	—
$+3$	—	—	—	—
$+4$	—	ClO_2	BrO_2	—
$+5$	—	—	—	I_2O_5
$+6$	—	Cl_2O_6	BrO_3 or Br_3O_9	—
$+7$	—	Cl_2O_7	—	—

Fluorine monoxide, F_2O, is a thermodynamically stable molecule with respect to the elements. It is a powerful oxidising agent. For example, it oxidises water with production of oxygen gas:

$$F_2O + H_2O \rightarrow O_2 + 2HF$$
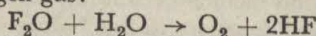
Chlorine monoxide which is prepared by treating HgO with Cl_2 gas is very unstable and decomposes with explosion into Cl_2 and O_2. Chlorine dioxide, ClO_2, which is prepared by the reduction of ClO_3^- with SO_2 is also unstable. Cl_2O_6 is obtained by the oxidation of ClO_2 with ozone and Cl_2O_7, by dehydrating $HClO_4$. All these oxides are powerful oxidising agents and explode when heated or subjected to a mechanical shock.

Bromine oxides are not very well characterised. I_2O_5 is formed by dehydrating iodic acid (HIO_3) at 200°C:

$$2HIO_3 \rightarrow H_2O + I_2O_5$$
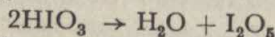
Iodine pentoxide is a stable compound and oxidises a number of reducing agents. I_2O_5 oxidises CO into CO_2. This reaction is used in the analysis of carbon monoxide:

$$5CO + I_2O_5 \rightarrow 5CO_2 + I_2$$
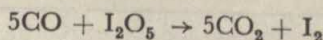
16.7.4 Oxy-acids

Oxy-acids of the halogens are listed in Table 16.16. Fluorine does not form any oxy-acid.

Hypohalous acids (HXO) are formed by the disproportionation of the halogens in water:

$$X_2 + H_2O \rightleftharpoons HXO + HX$$
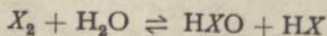
Hypohalous acids can also be prepared by passing halogens through an aqueous suspension of mercuric oxide:

$$2X_2 + 2HgO + H_2O \rightarrow HgX_2 \cdot HgO + 2HXO$$
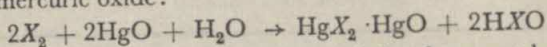
All these acids are very weak and unstable and thus have not been isolated in pure state.

Chlorous acid ($HClO_2$) in which chlorine is present in the $+3$ oxidation state, is prepared in the form of its sodium salt by the action of chlorine dioxide with Na_2O_2:

$$Na_2O_2 + 2ClO_2 \rightarrow 2NaClO_2 + O_2$$
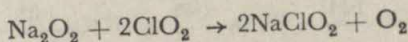
It is a moderately strong acid with a dissociation constant 10^{-2}.

Halic acids (HXO_3) are prepared by acidifying halites. Halites are formed by disproportionation of hypohalides in basic solution at about 70°C.

$$3XO^- \rightarrow XO_3^- + 2X^-$$
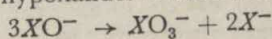
These acids are strong acids and dissociate completely in water. Chloric and bromic acids are not isolated in pure state but HIO_3 has been isolated as a white solid. Halic acids are powerful oxidising agents.

Perchlorates are prepared by the electrolytic oxidation of chlorates. In pure state, they react explosively with organic matter. Kinetically the reactions of perchloric acid are very slow. Perbromates have not been, until recently, prepared and isolated. However, there are recent claims that these have been made. Periodic acid exists in several forms. Its most important form is para-periodic acid (H_5IO_6) which is a weak acid. In this molecule, iodine atom is surrounded by five hydroxyl ions and one oxygen atom at the corners of an octahedron. It is also a very strong oxidising agent.

The structures of the various oxy-anions of chlorine are given in Fig. 16.20. The oxy-anions of bromine and iodine possess similar structures.

Fig. 16.20 The hypochlorite, chlorite, chlorate and perchlorate anions
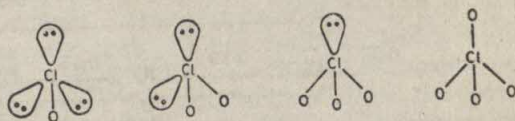
The solution chemistry of halogens has been extensively studied and it would be instructive to look into the standard electrode potentials for Cl_2, Br_2, I_2 and their compounds in acidic and alkaline solutions. These are summarised in Table 16.17. The values of electrode potentials show that these species are powerful oxidising agents, both in acidic and in basic solutions.

Table 16.16 Oxy-acids of Halogens

Oxidation state	Oxy-acids of		
	Chlorine	*Bromine*	*Iodine*
+1	HClO	HBrO	HIO
+3	HClO$_2$	—	—
+5	HClO$_3$	HBrO$_3$	HIO$_3$
+7	HClO$_4$	—	HIO$_4$
			H$_4$I$_2$O$_9$
			H$_5$IO$_6$

Table 16.17   Standard Electrode Reduction Potential Diagrams for Halogens and their Compounds(V)

Acid Solution

$$
\underset{\underset{\textstyle 1\cdot43}{\underbrace{\hspace{4.5cm}}}}{\overset{\overset{\textstyle 1.47}{\overbrace{\hspace{5cm}}}}{ClO^-_4 \xrightarrow{\,1\cdot19\,} ClO^-_3 \xrightarrow{\,1\cdot21\,} HClO_2 \xrightarrow{\,1\cdot65\,} HClO}} \xrightarrow{\,1\cdot63\,} \underset{\underset{\textstyle 1\cdot49}{\underbrace{\hspace{3cm}}}}{Cl_2} \xrightarrow{\,1\cdot36\,} Cl^-
$$

$$
\underset{\underset{\textstyle 1\cdot33}{\underbrace{\hspace{3cm}}}}{\overset{\overset{\textstyle 1.52}{\overbrace{\hspace{4cm}}}}{BrO^-_4 \xrightarrow{\,1\cdot76\,} BrO^-_3 \xrightarrow{\,1\cdot50\,} HBrO \xrightarrow{\,1\cdot60\,} Br_2}} \xrightarrow{\,1\cdot97\,} Br^-
$$

$$
H_5IO_6 \xrightarrow{\,1\cdot60\,} \underset{\underset{\textstyle 0\cdot99}{\underbrace{\hspace{4cm}}}}{\overset{\overset{\textstyle 1.20}{\overbrace{\hspace{3cm}}}}{IO^-_3 \xrightarrow{\,1\cdot13\,} HIO \xrightarrow{\,1\cdot45\,} I_2}} \xrightarrow{\,1\cdot54\,} I^-
$$

Alkaline Solution

$$
\underset{\underset{\textstyle 0\cdot50}{\underbrace{\hspace{4cm}}}}{\overset{\overset{\textstyle 0.63}{\overbrace{\hspace{6cm}}}}{ClO^-_4 \xrightarrow{\,0\cdot36\,} ClO^-_3 \xrightarrow{\,0\cdot33\,} ClO^-_2 \xrightarrow{\,0\cdot66\,} ClO^-}} \xrightarrow{\,0\cdot40\,} \underset{\underset{\textstyle 0\cdot89}{\underbrace{\hspace{3cm}}}}{Cl_2} \xrightarrow{\,1\cdot36\,} Cl^-
$$

$$
BrO^-_4 \xrightarrow{\,?\,} BrO^-_3 \xrightarrow{\,0\cdot54\,} \underset{\underset{\textstyle 0\cdot76}{\underbrace{\hspace{3cm}}}}{\overset{\overset{\textstyle 0.50}{\overbrace{\hspace{3cm}}}}{BrO^- \xrightarrow{\,0\cdot45\,} Br_2}} \xrightarrow{\,1\cdot07\,} Br^-
$$

$$
[H_3IO_6]^{2-} \xrightarrow{\,0\cdot7\,} IO^-_3 \xrightarrow{\,0\cdot14\,} \underset{\underset{\textstyle 0\cdot49}{\underbrace{\hspace{3cm}}}}{\overset{\overset{\textstyle 0.26}{\overbrace{\hspace{3cm}}}}{IO^- \xrightarrow{\,0\cdot45\,} I_2}} \xrightarrow{\,0\cdot54\,} I^-
$$
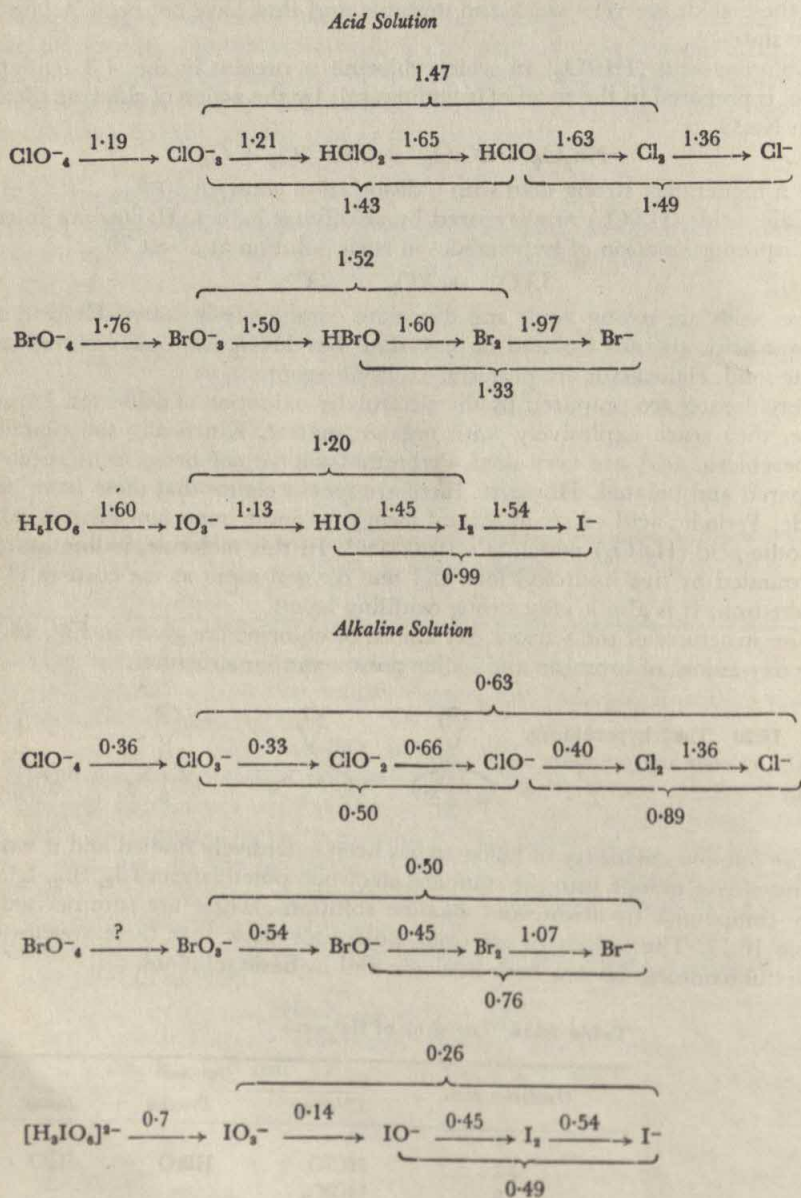
The E° values of HClO, HBrO, HIO, HClO$_2$, HClO$_3$ species indicate that these will disproportionate in acid solutions. In alkaline solution all the species except ClO$^-_4$, BrO$^-_4$, (H$_3$IO$_6$)$^{2-}$, Cl$^-$, Br$^-$, I$^-$ should disproportionate.

Example 16.12 Show how Cl_2 will disproportionate into Cl^- and ClO^- in basic solution.

In alkaline solution, the $E°$ values for this system are as follows:

$$ClO^- \xrightarrow{\ 0.40\ } Cl_2 \xrightarrow{\ 1.36\ } Cl^-$$

$$4\ OH^- + Cl_2 \longrightarrow 2\ ClO^- + 2\ H_2O + 2\ e \qquad E° = -0.40\ V$$
$$2\ e + Cl_2 \longrightarrow 2\ Cl^- \qquad\qquad\qquad\qquad E° = +1.36\ V$$

$$\overline{2\ OH^- + Cl_2 \longrightarrow ClO^- + H_2O + Cl^- \qquad E° = 0.96\ V}$$
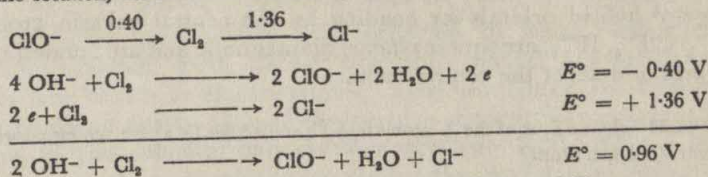
The value of $E°$ indicate that Cl_2 will disproportionate into ClO^- and Cl^-.

Example 16.13 On addition of free halogens to a hot concentrated solution of an alkali, the corresponding halide and halate ions are produced rather than the halide and hypohalite ions. Explain.

Any free halogen when added to an alkaline solution initially forms halide and hypohalite ions. We know from Example 16.12 that

$$Cl_2 + 2\ OH^- \rightarrow ClO^- + H_2O + Cl^- \qquad E° = 0.96\ V$$
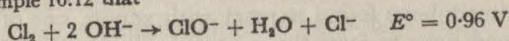
But, ClO^- ions, thus formed will be unstable to disproportionation to ClO_3^- and Cl^-.

$$4\ e + 2\ ClO^- + 2\ H_2O \rightarrow 2\ Cl^- + 4\ OH^- \quad E° = 0.89\ V$$
$$4\ OH^- + ClO^- \rightarrow ClO_3^- + 2\ H_2O + 4\ e \quad E° = -0.50\ V$$

Thus, $\qquad \overline{3\ ClO^- \rightarrow 2\ Cl^- + ClO_3^- \qquad\qquad E° = +0.39\ V}$
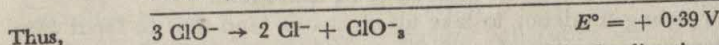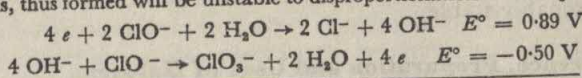
This positive value indicates that the reaction will proceed in the direction shown. Hence, Cl_2 when added to any alkali will give Cl^- and ClO_3^-.

16.7.5 Interhalogen Compounds

Halogens react with each other under suitable conditions of concentration, temperature and pressure to form a series of binary compounds of the formula XX'_n, where X and X' are different halogen atoms and n is 1, 3, 5, or 7. With $n = 1$, all the interhalogen compounds (XX') except IF are known. Other compounds are ClF_3, BrF_3, ICl_3, ClF_5, BrF_5, IF_5 and IF_7. All the interhalogen compounds are strong oxidising agents. The bonds in interhalogen compounds are essentially covalent because of the small electronegativity differences and the more electronegative atom acquires a formal negative charge.

The molecular structures of these compounds are very interesting. ClF_3, BrF_3, and ICl_3 are T-shaped molecules (Fig. 16.21). In these molecules, the central atom is sp^3d hybridised (trigonal bipyramid). Two of the five orbitals (equatorial) contain two lone pairs of electrons and the other three (two axial, one equatorial) are used to form bonds with the other three atoms of halogens. In XX'_5, the central atom X is sp^3d^2 hybridised. One of the hybridised orbitals (axial)
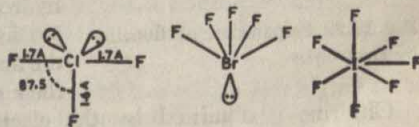
Fig. 16.21 Some interhalogen compounds (ClF_3, BrF_5 and IF_7)

has a lone pair of electrons while the other five are used in bonding with X', thus, giving a distorted square-pyramidal shape to the molecule. The four X' atoms are slightly above the equatorial-plane which has the central atom X (Fig. 16.21). XX'_7 molecules have the shape of a pentagonal bipyramid and the seven X' atoms are bonded through d^3sp^3 hybrid orbitals of X.

All neutral interhalogen molecules are diamagnetic indicating no unpaired electrons. Uninegative interhalogen ions, like ICl^-_2, IBr^-_2, $BrCl^-_2$ having an odd number of halogen atoms are known. These are also diamagnetic and T-shaped, utilising dsp^3 hybrid orbitals for bonding by the central halogen atom. Ions like ICl^-_4, ClF^-_4, IF^-_4, are square planar, diamagnetic and are bonded through d^2sp^3 hybrid orbitals of the central atom.

Example 16.14 Why do four of the X' atoms in XX'_5 molecules lie above the equatorial plane having central halogen atom?

The X atom in all the XX'_5 molecules have one non-bonded electron pair directed along the axis. One knows that non-bonded–bonded electron pair repulsion is more than bonded–bonded electron pair repulsion (see Chapter 4). Therefore, owing to the larger repulsion between non-bonded–bonded electron pairs (compared to bonded pairs) the four X' atoms lie above the plane.

Interhalogen compounds are generally more reactive than the halogens. Fluorine has recently been found to react with xenon, one of the noble gases, under various conditions to form the crystalline solids XeF_2, XeF_4 and XeF_6, which are reasonably stable.

16.7.6 Occurrence, Preparation and Uses of Halogens

Because of their strong tendency to take up electrons (and thus to form compounds), halogens are never found in the free state in nature. Fluorine occurs in the combined state as *fluorspar*, CaF_2 and *cryolite*, Na_3AlF_6. Chlorine is found as Cl^- in water soluble salt deposits (such as NaCl) and in salt waters. Bromide occurs mainly as sodium, potassium, and magnesium salts, which are obtained from brine wells and sea water. The principal sources of iodine are the sodium iodate and periodate that occur as impurities in the nitrate deposits (*saltpetre*) of northern Chile.

Since fluorine is itself the strongest of chemical oxidising agents, it is evident
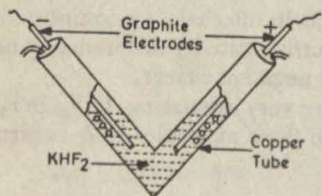
Fig. 16.22 Preparation of fluorine by electrolysis

that it would be difficult to prepare fluorine from fluorides. The common way to produce fluorine is by the electrolysis of fused potassium hydrogen fluoride, KHF_2 (Fig. 16.22). The electrolysis is carried out in anhydrous medium. (F^- cannot be oxidised in the presence of water because OH^- does.) The hydrogen liberated at the cathode is prevented from mixing with the fluorine liberated at the anode by means of a diaphragm (to prevent their explosive combination).

Chlorine is obtained by the electrolysis of an aqueous sodium chloride solution. When such a solution is electrolysed, chlorine gas is set free at the anode, and hydrogen gas and hydroxide ion are produced at the cathode (see Chapter 12).

Bromine is obtained from sea water by the oxidation of bromide.

$$Cl_2 + 2\,Br^- \rightarrow Br_2 + 2\,Cl^-$$
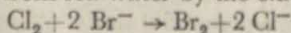
The bromine is absorbed in Na_2CO_3 solution, giving a mixture of NaBr and $NaBrO_3$, which when acidified and distilled gives bromine.

$$HBrO_3 + 5HBr \rightarrow 3\,Br_2 + 3H_2O$$
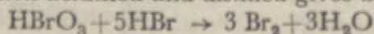
A commercial source of free iodine is the reduction of sodium iodate by means of sodium hydrogen sulphite:

$$2IO^-_3 + 5HSO^-_3 \rightarrow 5SO^{2-}_4 + 3H^+ + I_2 + H_2O$$
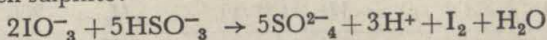
Fluoride ion, used widely in fluorination of water, under controlled conditions, inhibits tooth decay. Covalently bound fluorine–carbon compounds are known as fluorocarbons. These substances are very inert and strong oxidising agents. One of the popular commercial products containing fluorine is the polymer polytetrafluoroethylene $(CF_2—CF_2)_n$, known as *teflon*. Its great thermal stability has made teflon useful as a coating material. Some of the fluorinated methane derivatives are used as refrigerants.

Chlorine is one of the important industrial chemicals. Its major use is as a bleaching agent, especially for wood pulp and paper; it is also used for bleaching cotton cloth. Chlorine is used in the production of bleaching powder and in the disinfection of water supplies. Solutions of NaOCl are used as household laundry bleaches. Potassium chlorate is used as the oxidising agent in match-sticks and fire works.

The most important commercial use of bromine is as silver bromide, one of the components of photographic emulsions. Exposure to light causes silver bromide to break down into free silver resulting in the dark areas of a negative photograph. Bromine is also used in the production of ethylene dibromide, $C_2H_4Br_2$, which is added to petroleum containing the antiknock additive tetraethyl lead. In the process of burning petroleum, lead is produced from the additive. Lead would deposit in the engine if ethylene dibromide were not present. In the presence of ethylene dibromide, lead is converted into lead bromide, which is eliminated in the exhaust.

The most important use of iodine is as an antiseptic. A solution of iodine in ethyl alcohol, known as *tincture of iodine* is marketed for home use. Iodine is also used in the preparation of a number of metal iodides and organic compounds.

16.8 HYDROGEN

The hydrogen atom is the simplest of all atoms with a nucleus of $+1$ charge and a single electron in the $1s$ orbital. Owing to its unique simple structure, hydrogen exhibits certain properties special to itself. In its properties hydrogen resembles the elements of both group IA and group VIIA. This is due to the fact that it may either lose its single valence electron as do group IA elements, or gain an electron in its valence shells as halogens do to attain a noble gas configuration. Although hydrogen is not exceptionally reactive, it forms more compounds than any other element.

Hydrogen exists as a diatomic covalently bonded molecules. It is highly stable and its dissociation (atomisation) requires a large amount of energy (104 kcal mol^{-1}). The dissociation can be affected by passing the gas through a source having energy equivalent to or more than that required for dissociation, e.g. electric arc or very high temperature. The ionisation potential of hydrogen is very high compared to the first ionisation potentials of most other elements. Compounds of hydrogen with most elements, therefore, involve covalent bonds. For example, hydrogen chloride has a bond energy of 103 kcal mol^{-1}. For a purely ionic bond between H^+ and Cl^-, we should expect a bond energy of -34 kcal mol^{-1} as shown in the following:

$$\begin{array}{llll}
\text{H}(g) & \rightarrow \text{H}^+(g)+e & \Delta H_1 = +313 \text{ kcal mol}^{-1} \\
\text{Cl}(g)+e & \rightarrow \text{Cl}^-(g) & \Delta H_2 = -87 \text{ kcal mol}^{-1} \\
\text{H}^+(g)+\text{Cl}^-(g) & \rightarrow \text{H}^+ - \text{Cl}^-(g) & \Delta H_3 = -260 \text{ kcal mol}^{-1} \\
\hline
\text{H}(g)+\text{Cl}(g) & \rightarrow \text{HCl}(g) & \Delta H = -34 \text{ kcal mol}^{-1}
\end{array}$$
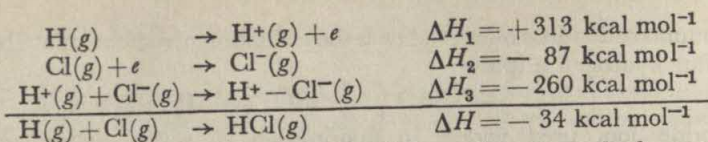
We see that even for a molecule like HCl, formed between hydrogen and a highly electronegative element like chlorine, there has to be a certain amount of covalent character in the bond.

The hydrogen ion is smallest in size and thus it has a very large charge to radius ratio. This high ratio results in great distortion of the electron cloud surrounding other atoms with which H^+ interacts; H^+ does not, therefore, exist in the free state, but in combination with other species such as the solvent:

$$\begin{array}{lll}
\text{H}^+ + \text{H}_2\text{O} & \rightarrow & [\text{H}_3\text{O}]^+ \\
\text{H}^+ + \text{H}_2\text{SO}_4 & \rightarrow & [\text{H}_3\text{SO}_4]^+ \\
\text{H}^+ + \text{HF} & \rightarrow & [\text{H}_2\text{F}]^+ \\
\text{H}^+ + \text{Cl}^- + \text{H}_2\text{O} & \rightarrow & [\text{H}_3\text{O}]^+ + \text{Cl}^-
\end{array}$$
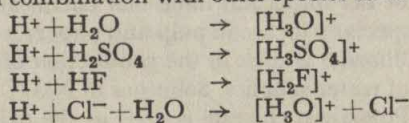
The hydrogen atom can accept an electron from other elements to form the hydride ion, H^-:

$$\text{H} \cdot + e \rightarrow \text{H}^- \qquad \Delta H = -18 \text{ kcal mol}^{-1}$$
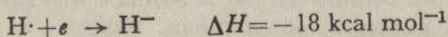
The formation of the hydride ion indicates that hydrogen can be grouped with halogens, but the tendency for hydrogen to form the hydride ion is much less than the tendency of any of the halogens to form the halide ion:

$$\begin{array}{lll}
e + \tfrac{1}{2}\text{H}_2 & \rightarrow \text{H}^- & \Delta H = +36 \text{ kcal mol}^{-1} \\
e + \tfrac{1}{2}\text{Br}_2 & \rightarrow \text{Br}^- & \Delta H = -55 \text{ kcal mol}^{-1}
\end{array}$$
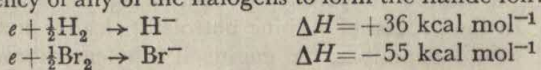
The formation of hydride ion from hydrogen molecule is an energy-consuming process and, therefore, the ion can be formed only with those elements which have low ionisation energies (and can form ionic hydrides) like the alkali and alkaline earth metals. The properties of many of these hydrides have been already discussed in previous sections.

Another manner by which hydrogen combines with other elements is by forming electron pair bonds, e.g. in H_2, HCl, NH_3, or CH_4. These are the covalent hydrides, the largest family of which is that of carbon, discussed earlier in Chapters 5, 14 and 15.

Besides these, there are other properties which are unique to hydrogen, some of which are listed below. (These properties have been discussed in other chapters.)

(*i*) Formation of hydrogen bond (Chapter 8).

(*ii*) Formation of hydrogen bridge bond in electron deficient compounds, such as in boron hydrides (see section 16.3).

(*iii*) Formation of compounds where transition metal ions are directly bonded to hydrogen as in $HCo(CO)_4$ (Chapter 17).

Hydrogen reacts with carbon monoxide at high temperatures in the presence of a catalyst to produce CH_3OH. This process is used industrially to manufacture methyl alcohol.

$$2\text{H}_2 + \text{CO} \rightarrow \text{CH}_3\text{OH}$$
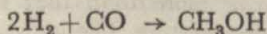
Hydrogen is a good reducing agent and reacts with metal oxides to form pure metals.

$$\begin{array}{lll}
\text{CuO}(s) + \text{H}_2(g) & \rightarrow & \text{Cu}(s) + \text{H}_2\text{O}(g) \\
\text{FeO}(s) + \text{H}_2(g) & \rightarrow & \text{Fe}(s) + \text{H}_2\text{O}(g) \\
\text{WO}_3(s) + 3\text{H}_2(g) & \rightarrow & \text{W}(s) + 3\text{H}_2\text{O}(g)
\end{array}$$
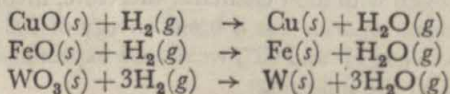
Such reactions are employed in metallurgical processes. For example, tungsten is commercially obtained by the reduction of WO_3 by hydrogen.

16.8.1 Isotopes of Hydrogen

There are three isotopes of hydrogen: ^1_1H, which constitutes approximately 99·985 per cent of the naturally occurring hydrogen, *deuterium*, ^2_1H or (^2_1D), or heavy hydrogen constituting 0·015 per cent and the radioactive *tritium*, ^3_1H or (^3_1T) which occurs only in trace amounts (1 part in 10^7). The chemical properties of these isotopes are essentially identical, but the rates and equilibrium constants of their reactions are appreciably different due to both the mass and nuclear effects. Owing to the existence of these isotopes, natural hydrogen can exist as H_2, HD, HT, D_2, T_2, and DT.

Water containing heavy hydrogen (^2_1D) is known as heavy water, D_2O. It boils at 101·42°C and freezes at 3·82°C as compared with 100°C and 0·00°C, respectively for ordinary water, H_2O. Heavy water can be separated from the naturally occurring water by any of the methods of fractionation, e.g. fractional distillation.*

16.8.2 'Ortho'-and 'Para'-hydrogen

Molecular hydrogen exists in two forms—*ortho-* and *para*-hydrogen—because the nucleus of a hydrogen atom has a non-zero spin. In the hydrogen molecule, the nuclear spins of the two hydrogen atoms can be in the same direction (*ortho*) or in the opposite directions (*para*) as shown in Fig. 16.23. *Ortho* and *para* varieties exist for all symmetrical diatomic molecules but apart from H_2 and D_2 none of the other pairs exhibit appreciable chemical differences. An equilibrium mixture of hydrogen at room temperature contains 75 per cent *ortho* and 25 per cent *para* forms, but at lower temperature (around 20 K), practically pure *para* hydrogen can be obtained. The two forms differ slightly in their thermal conductivities, specific heats, vapour pressure, and melting and boiling points.

Ortho   Para
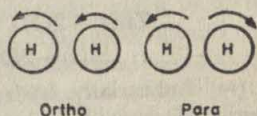
Fig. 16.23 *Ortho*- and *para*-hydrogens

16.8.3 Occurrence and Preparation of Hydrogen

Hydrogen constitutes about 1 per cent of the earth, water and the atmosphere, and ranks ninth in the order of abundance of elements. It is found mostly in the combined state (e.g. water, hydrocarbons). Free hydrogen occurs in earth only in very small amounts.

Hydrogen can be prepared by any one of the following methods.

(*i*) By the action of water or acids on elements whose standard oxidation potential is positive (e.g. Na, K, Ca, Mg):

$$2Na(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2(OH^-)(aq) + H_2(g)$$
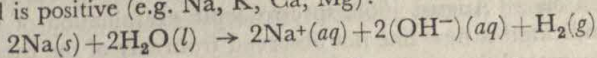
or, in general, $M + nH^+ \rightarrow M^{n+}(aq) + \dfrac{n}{2} H_2(g)$

The temperature of the above reaction will vary with the reactivity or the rate of reaction of the metals.

*In India D_2O is manufactured at Nangal, near Chandigarh, by the electrolysis of water. D_2O is poisonous because it slows down the rates of the reactions occurring in the human body.

(*ii*) Coke and steam react at high temperatures (1000°C) to produce water gas:

$$C(s) + H_2O(g) \rightarrow \frac{CO(g) + H_2(g)}{\text{water gas}}$$
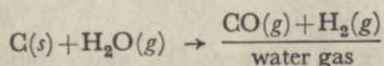
Water gas is mixed with steam and passed over a catalyst at 500°C whereby carbon monoxide is converted to carbon dioxide:

$$H_2(g) + CO(g) + H_2O(g) \rightarrow CO_2 + 2H_2(g)$$
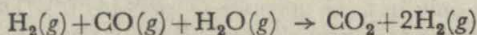
Carbon dioxide is separated from hydrogen by dissolving it in cold water under pressure.

(*iii*) Hydrogen can also be obtained by the catalytic decomposition of hydrocarbons at high temperatures:

$$C_2H_6 \rightarrow 2C(s) + 3H_2(g)$$
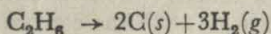
In petroleum refineries hydrocarbons having higher molecular masses are decomposed into hydrocarbons of lower molecular masses (*cracking* process); in this process hydrogen is produced as a by-product.

(*iv*) Very pure hydrogen is prepared by the electrolytic decomposition of water containing a small amount of acid or alkali:

$$2H_2O \rightarrow 2H_2(g) + O_2(g)$$
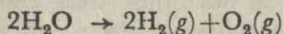
(*v*) Certain metals and non-metals displace hydrogen from alkaline solutions.

$$Zn(s) + 2OH^-(aq) + 2H_2O \rightarrow [Zn(OH)_4]^{2-}(aq) + H_2(g)$$
$$Si(s) + 2OH^-(aq) + H_2O \rightarrow SiO^{2-}_3(aq) + 2H_2(g)$$
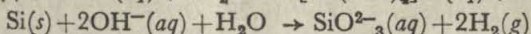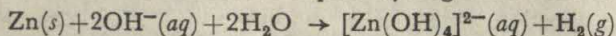
(*vi*) Industrially, hydrogen gas is obtained as a by-product in the industrial preparation of sodium hydroxide by the electrolysis of aqueous sodium chloride.

$$2Na^+(aq) + 2Cl^-(aq) + 2H_2O \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g) + Cl_2(g)$$
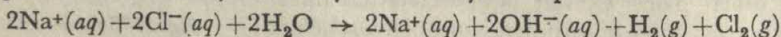
Hydrogen is a nonpolar, colourless, tasteless gas, having the lowest density of all the elements. It is a diatomic molecule with a weak interaction between molecules. This weak force of attraction is indicated by its very low melting point (−259·1°C) and low boiling point (−252·7°C). It is highly insoluble in water.

16.9 NOBLE GASES

This group of less reactive elements (He, Ne, Ar, Kr, Xe, Rn) has a very interesting history behind its discovery. It dates as far back 'as the eighteenth century when the study of gases was at its peak. Cavendish, while passing an electric discharge in a mixture of air and oxygen to prepare oxides of nitrogen and then removing them and oxygen completely, discovered that there always remained a gaseous residue (1/120 of the original volume of air) which he thought might be a new element. After a lapse of a few years, during a total eclipse of the sun on 18 August 1868, spectroscopic examination of the sun's chromosphere indicated a new line not observed from any of the then known elements. This suggested the presence of a new element in the sun and the name 'helium' from the Greek word 'helios' (meaning sun), was given to it. Ramsay in 1895, while making a spectroscopic examination of a gas obtained from the mineral *clevite*, observed the helium lines which were later confirmed by Crooks and Lockyer thus establishing the presence of the element on the earth also. Helium was finally isolated from the atmosphere by Ramsay and Travers in 1900. During the same year, Rayleigh, along with Ramsay, published results

of the isolation of another new element from the atmosphere.* The new element was a monatomic gas, chemically inert, with an atomic mass of 39·9. They named it 'argon' (the lazy one), because of its inert character. In the next four years other gases, namely, krypton, xenon and neon were also isolated by Ramsay and Travers. The extension of the periodic table with the discovery of polonium and radium suggested that there should be one more element having properties similar to those of the inert gases. In 1902, Rutherford and Soddy succeeded in condensing radon by means of liquid air which was proved to be the heaviest member of the noble gas family by Ramsay and Gray. This group of elements are generally called *noble gases, inert gases,* or *rare gases*; the first two names were given because of the apparent absence of reactivity and the last name due to their rarity.

The noble gases occur in relatively small amounts in the atmosphere. Helium is present in certain natural gases which must have originated from the decay of radioactive elements. Helium is also found as the occluded gas in some of the radioactive minerals and can be released on heating. The other rare gases (neon, argon, krypton and xenon) are obtained by fractional distillation of liquid air.

16.9.1 Properties

Noble gases form a family of elements because their physical and chemical properties are similar. Most of their physical properties are given in Table 16.18. They are all colourless, tasteless and odourless monatomic gases.† All have valence shells which are closed octets. This accounts for their inert nature. The elements form low boiling liquids, the boiling points decreasing rapidly with the decrease in molecular mass. Helium has the lowest boiling and melting point. It crystallises in a hexagonal closed packed (HCP) structure while neon, argon, xenon and krypton crystallise in cubic closed packed (FCC) structure. Since there are no unpaired valence electrons in these elements, this difference in crystal structure can only arise from the difference in the van der Waals forces. The physical properties of these gases like the refractive index, dielectric constant, diamagnetic susceptibility, heat capacities and polarisability, are essentially due to those of individual atoms.

Liquid helium has some peculiar properties not possessed by any other substance known. Thus, liquid helium, He(I), at 4·12 K is a normal liquid, but on cooling to 2·178 K, another allotrope of helium, called helium (II), appears. The transition from He(I) to He(II) is accompanied by a sharp transition in physical properties (see Chapter 10 for the phase diagram of helium). The viscosity of He(II) is negligible. Liquids with such low viscosity are known as *superfluids*; there is effectively no resistance to their flow. Therefore, when kept in a container helium even goes uphill and flows out of the vessel. This state of He(II) is sometimes referred to as the fourth state of matter.

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*Rayleigh was the first to note that nitrogen prepared from decomposition of compounds was of lower density (1·2505 g per litre at STP) than the gas residue obtained from air after removing O_2, CO_2 and H_2O (1·2572 g per litre). Even in modern times, many may have ignored this small difference in densities. The amazing skill, originality and vision of this early study are truly remarkable.

†There is some spectroscopic evidence that under special conditions a small proportion of the diatomic noble gas molecules are present in all gases except helium.

Table 16.18 Properties of the Noble Gases[1]

Property	Element					
	Helium	Neon	Argon	Krypton	Xenon	Radon
Atomic number	2	10	18	36	54	86
Electron configuration	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6$	$4s^2 4p^6$	$5s^2 5p^6$	$6s^2 6p^6$
Atomic mass	4·0026	20·183	39·948	83·80	131·30	(222)
Boiling point, °C	−268·9	−246·1	−185·9	−153·4	−108·1	−62·0
ΔH_{vap}, kcal mol^{-1}	0·022	0·44	1·50	2·31	3·27	4·3
Solubility in water[2]	8·61	10·5	33·6	59·4	108·1	—
First ionisation energy, kcal mol^{-1}	576·2	497·3	363·5	322·9	279·8	248·0
Second ionisation energy, kcal mol^{-1}	1254·8	947·3	637·1	566·5	489·2	—
Crystal structure	HCP	FCC	FCC	FCC	FCC	FCC
Atmospheric content, % vol	$5·24 \times 10^{-4}$	$1·82 \times 10^{-3}$	0·934	$1·14 \times 10^{-3}$	$8·7 \times 10^{-6}$	—

[1]For explanation of the symbols in the table, refer to Table 16.1.
[2]cc per 1000 g of H_2O at 25°c and 1 atm pressure:

The solubility of noble gases in water is much more than that of oxygen or nitrogen. It increases with the increase in atomic mass of the element. The solubility is due to dipole-induced dipole interaction; the noble gas with larger atoms being more polarisable is also more soluble than a gas with smaller atoms.

The noble gases have been of use (*i*) in arc welding and cutting, (*ii*) for maintaining inert atmosphere in metallurgical and other studies, (*iii*) as filler gases in the electronic and lighting industry, (*iv*) in cryogenics (low-temperature science), and (*v*) in experimental nuclear physics. Helium, being light and non-inflammable, is used to fill weather balloons and air-ships. Helium is used extensively for attaining low temperatures. The most important use of radon is in the treatment of cancer.

16.9.2 Compounds of Noble Gases

The compounds prepared prior to 1962 were only very weakly bonded species like *clathrate* compounds and some short-lived species. In clathrates the bonds are neither ionic nor covalent, but mostly of van der Waals type. However, since 1962, several stable compounds of xenon, krypton and radon with fluorine and oxygen have been prepared.* Recently, it has been shown that xenon also forms xenon dichloride.

The most easily prepared compounds of the noble gases are *clathrate* compounds in which the noble gas molecules are trapped in the cavities in the crystalline lattices of suitable organic or inorganic compounds. The hydrates were the first member of this group of compounds. Typical examples of clathrates are $X(2N)$ $17H_2O$ where N stands for the noble gas (Ar, Xe, or Kr) and

*The preparation of stable noble gas compounds is a landmark in chemistry. Noble gases which were considered to be inert (and were even called inert gases) for years, lost their inertness in 1962.

Table 16.19 Important compounds of Xenon

$XePtF_6$; $Xe(PtF_6)_2$; $XeRuF_6$; $XeRhF_6$; $XePuF_6$; XeF_2; XeF_4; XeF_6; XeO_3; $XeOF_2$; XeF_4; XeF_8; XeO_2; $XeOF_2$; $XeOF_3$; $XeOF_4$; XeO_2F_2; XeO_2F_4; XeO_3F_2; H_4XeO_6; Na_4XeO_6; $Xe(OH)_6$; Na_6XeO_6; K_4XeO_6; Ba_2XeO_6; $XeF_2 \cdot 2TaF_5$; $Xe \cdot 2SbF_5$; KrF_2; KrF_4; RnF_4; $Xe(TaF_6)_2$; $Xe(NbF_6)_2$; $XeTaF_7$; $XeNbF_7$; $CsFXeF_6$; $2CsFXeF_6$; $RbFXeF_6$; $2RbFXeF_6$; $2KFXeF_6$; $2NaFXeF_6$; AsF_5XeF_6; VF_5XeF_6; $BFXeF_6$; $2SbF_5XeF_6$; SbF_5XeF_6; SbF_5XeF_6; $SnF_4 \cdot 4XeF_6$; $2NoFXeF_6$; $No_2F \cdot XeF_6$; $GeF_4 \cdot 4XeF_6$; $GeF_4 \cdot 2XeF_6$; $GeF_4 \cdot XeF_6$; $XeCl_2$; XeO_4.

$X = CH_3COOH$, CH_2Cl_2, $CHCl_3$ or CCl_4. In such compounds, the water molecules provide the host lattice. The other compounds which form host lattices are quinone (o-dihydroxybenzene), and phenol. The bonding in clathrates involves only van der Waals forces, also termed as dispersion forces. The organic or water molecules form a cage which traps the rare gas atoms.

In 1962, Neil Bartlett published the first valid account of a true chemical reaction between xenon and platinum hexaflouride. This success was based on the argument that since O_2 reacts with PtF_6 to form O_2^+ PtF_6^-, and since the ionisation potentials of O_2 and Xe are the same (12 eV), this reaction should occur with Xe also. This work was followed by synthesis of a variety of xenon compounds and of several radon and krypton compounds. All these compounds involve chemical bonds between noble gas atoms and the most electronegative elements like fluorine and oxygen. No compounds of helium and argon have yet been prepared.

Stable compounds have been isolated for xenon in which it exhibits even oxidation states ($+2$, $+4$, $+6$

Fig. 16.24 Flow chart of the reactions of XeF_2 and XeF_4

and $+8$). It forms three types of compounds: (*i*) fluorides, (*ii*) oxyflourides, and (*iii*) oxides called xenates and perxenates. The list of xenon compounds is given in Table 16.19. The methods of preparation of the xenon fluorides and their important physical properties are given in Table 16.20. Chemical properties of two fluorides are shown in Fig. 16.24.

16.9.3 Structure and Bonding in Xenon Compounds

It may appear that some special bonding scheme would be necessary to explain the formation of bonds between xenon and fluorine or oxygen (see Fig. 16.25 for shapes of some of these molecules). However, such is not the case; the principles applied to explain the bonding in these compounds are essentially the same as those in other chemical compounds. There is close analogy between the polyhalides like, ICl_2^-, ICl_4^- and IF_6^- and xenon halides with regard to bonding structures. We will describe briefly the molecular orbital approach to these structures.

Table 16.20 Xenon Fluorides

Compound	Method of preparation	Properties
XeF_2	(1) Sealed tube reaction between Xe and F_2 (1 : 3 ratio). (2) Passing a hot mixture of Xe and F_2 (1 : 2) over a nickel tube. (3) Heating Xe with CF_3OF. (4) Electric discharge (600 V) at $-78°C$ of a mixture of Xe and CF_4 or SiF_4.	Colourless solid (vap. pressure 3 mm at 25°C) with a melting point 120–140°C, density 4·32 g cc^{-1}, and soluble in HF. $\Delta H_f = -37$ kcal mol^{-1}, bond energy 30 kcal mol^{-1}. Quite stable.
XeF_4	(1) Heating Xe with F_2 (1 : 5) in a sealed Ni tube at high pressures. (2) An electric discharge (1000–3000 V) of a mixture of Xe and F_2 (1 : 2)	Colourless solid (vap. pressure 3 mm at 25°C), with a melting point of 100°C, density, 4·42 g cc^{-1}, and soluble in C_7F_{16}, HF and benzene. $\Delta H_f = -53$ kcal mol^{-1}, bond energy 31 kcal mol^{-1}. Stable up to 140°C under N_2.
XeF_6	(1) Irradiation of a mixture of Xe and F_2 by 10 MeV protons. (2) Heating a large excess of F_2 with Xe in a tube at high pressure.	Colourless solid of the same vapour pressure as above, with a melting point of 46°C, soluble in HF, ionises and unstable.

Xenon fluoride contains one atom of xenon and two atoms of fluorine. In its simplest form, one can make molecular orbitals, using the p orbitals. One can combine one $5p_z$ orbital of xenon and two $2p_z$ orbitals of fluorine (one from each fluorine atom) and form three delocalised orbitals—one bonding, one non-bonding and one antibonding. There are four elecrons (two in $5p_z$ orbitals of xenon and one in each of the two p_z orbitals of fluorine) to be distributed in these three orbitals. Two electrons occupy the bonding orbital and the remaining two go to the non-bonding orbital

Such models can be extended to XeF_4 and XeF_6. The description of XeF_4 starts with four $2p$ orbitals (one from each fluorine) and one $5p$ orbital of xenon forming five delocalised molecular orbitals (two bonding, one non-bonding and two antibonding). Six electrons are to be distributed in these orbitals which go in the bonding and non-bonding orbitals. Similar is the case of XeF_6.

If we want to use the valence bond method to explain the bonding in XeF_2, we first construct the hybrid orbitals ($5p^3 6s 5d^2$) on xenon. Out of these, two diagonally opposite hybrid orbitals are used to overlap with the two p_z orbitals

XeF₂ (linear)   XeF₄(square planar)   XeF₆(distorted octahedral)

XeO₃ (pyramidal)   XeO₄(tetrahedral)   XeOF₄ (square pyramid)
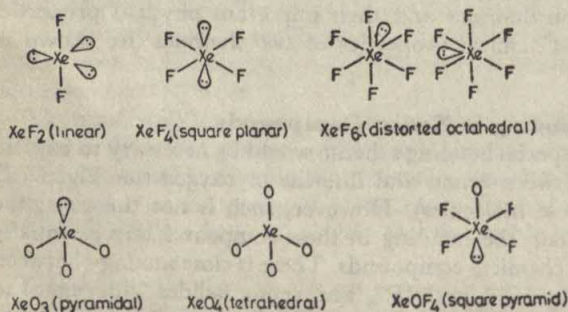
Fig. 16.25 Structures of some xenon compounds

Fig. 16.26 Bonding in xenon difluoride

on fluorine atoms (one from each fluorine atom) to form two electron pair bonds (Fig. 16.26).

Similarly in XeF_4 and XeF_6, the respective bonds are formed by the overlap of four $5p^3 5d^2 6s$ hybrid orbitals of xenon and four $2p$ orbitals of fluorine, and six $5p^3 5d^2 6s$ hybrid orbitals of xenon and six $2p$ orbitals of fluorine respectively.

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PROBLEMS

16.1 How would you expect the following properties of francium to compare with those of the other alkali metals (*i*) ionic radius, (*ii*) ionisation energy, (*iii*) oxidation potential, and (*iv*) melting point.

16.2 The standard reduction potentials of Li, Na and K are -3.05 V, -2.71 V and -2.93 V respectively. From this list pick out (*i*) the best reducing agent, (*ii*) the best oxidising agent, (*iii*) the poorest reducing agent, and (*iv*) the poorest oxidising agent.

16.3 Why are rubidium and caesium preferred over other alkali metals for use in photoelectric cells?

16.4 Account for the following facts: (*i*) $BeSO_4$ is soluble, but $BaSO_4$ is insoluble; (*ii*) $Be(OH)_2$ is insoluble, but $Ba(OH)_2$ is soluble.

16.5 On heating, calcium carbonate and magnesium carbonate readily form CaO and MgO respectively. Would Na_2CO_3 and $BaCO_3$ form the corresponding oxides on being heated to the same temperature? Explain.

16.6 How does each of the following properties affect the solubility: (*i*) high lattice energy, (*ii*) high hydration energy, (*iii*) low lattice energy, and (*iv*) low hydration energy?

16.7 (*i*) List the hydroxides of the alkaline earth metals in the order of increasing basicity. (*ii*) Arrange the following compounds in order of decreasing ionic character: $CaCl_2$, $BeCl_2$, $MgCl_2$, $BaCl_2$, and $SrCl_2$.

16.8 Account for the following: (*i*) the melting and boiling points of boron are higher than those of aluminium, (*ii*) aluminium hydroxide is amphoteric in nature, (*iii*) aluminium acts as a good reducing agent, (*iv*) the first ionisation energies of boron and aluminium are lower than those of beryllium and magnesium. (*v*) boron does not exist as B^{3+} cation in its compounds.

16.9 Suggest reasons why aluminium forms $+3$ ions in aqueous solution, but not $+1$ or $+2$ ions.

16.10 Why is aluminium stable in air and water?

16.11 Why do the heavier members of the group IIIA exhibit a valence of $+1$?

16.12 Why are certain metallic oxides reduced with aluminium rather than with carbon?

16.13 Contrast the structure and properties of SiO_2 and CO_2.

16.14 Why are carbon tetrachloride and silicon tetrachloride very different in their chemical behaviour?

16.15 Complete the following equations:

   (i) $P_4 + O_2 \longrightarrow$

   (ii) $As_4 + Cl_2 \longrightarrow$

   (iii) $SbCl_3 + H_2O \longrightarrow$

   (iv) $As_2O_3 + H_2O \longrightarrow$

   (v) $PCl_5 + H_2O \longrightarrow$

   (vi) $H_3AsO_4 + NaOH \longrightarrow$

16.16 Explain the low chemical reactivity of molecular nitrogen.

16.17 Silicon melts at 1400°C and white phosphorus at 44°C. Explain this large difference in terms of the structures of the solids.

16.18 Explain the following: (i) water has a higher boiling point than hydrogen sulphide; (ii) water is a weaker acid than hydrogen sulphide; (iii) the bond angle in water molecule is greater than in hydrogen sulphide; and (iv) water is thermally more stable than hydrogen sulphide.

16.19 Why is elementary oxygen a better oxidising agent than elementary sulphur?

16.20 Arrange the following groups of compounds in the decreasing order of the property indicated:

   (i) F_2, Cl_2, Br_2, I_2 Melting point

   (ii) F_2, Cl_2, Br_2, I_2 Reactivity

   (iii) HF, HCl, HBr, HI   Acid strength (in water)

   (iv) HF, HCl, HBr, HI   Bond energy

   (v) HF, HCl, HBr, HI   Heat of formation

   (vi) F_2, Cl_2, Br_2, I_2 Bond energy

16.21 The H—X bond in HF is more polar than in any of the other halogen halides. Why is the H—F bond the least ionised of all the hydrogen halides in dilute aqueous solution?

16.22 Complete and balance the following reaction equations:

   (i) $Fe^{3+} + Br_2 \longrightarrow$

   (ii) $SO_2 + H_2O + Br_2 \longrightarrow$

   (iii) $MnO_2 + H^+ + Cl^- \longrightarrow$

   (iv) $I_2 + S_2O_3^{2-} \longrightarrow$

   (v) $I_2 + H_2S \longrightarrow$

   (vi) $FeCl_2 + Cl_2 \longrightarrow$

16.23 Would you expect the addition of an electron to an atom with atomic number 35 to release or absorb energy? Explain the basis for your answer.

16.24 Which of the halogens (i) has the lowest melting point, (ii) has the largest atomic number, (iii) is present in bleaching powder, (iv) is obtained commercially in large quantities from sea water, (v) is the weakest oxidising agent, (vi) is easiest to oxidise, (vii) has to complete shells of electrons below the valence shell, (viii) decomposes water with the evolution of ozone, (ix) gives a weak acid when its hydrogen compound is dissolved in water, and (x) has the most extensive and varied commercial uses.

16.25 Since $HCl(g)$ can be prepared from NaCl and H_2SO_4, why is it that the reaction of NaBr and H_2SO_4 cannot be used to prepare HBr (g)?

16.26 Boron nitride, BN, exists in two crystalline modifications (i) diamond-like and (ii) graphite-like. Draw the structures of these nitrides.

16.27 Write equations for the following:

$NH_3 + Ag^+(aq) \longrightarrow$

$NH_3(g) + O_2(g) \longrightarrow$

$NH_3(g) + O_2(g) \xrightarrow{\text{(Pt catalyst)}}$

$NH_3(l) + Na(s) \longrightarrow$
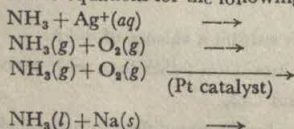
16.28 The melting and boiling points as well as the heats of vapourisation of the noble gases are lower than any other class of substances having comparable molecular mass. Why?

16.29 Complete the following equations:

(*i*) $XeF_4 + H_2O \longrightarrow$

(*ii*) $XeF_6 + H_2O \longrightarrow$

(*iii*) $XeF_6 + HF \longrightarrow$

(*iv*) $XeF_6(liquid) + CsF \longrightarrow$

(*v*) $XeF_6 + SiO_2 \longrightarrow$

16.30 What is helium-II?

16.31 Xenon hexafluoride dissolves in HF to form a solution which conducts electricity. There are two following possible modes of dissociation of XeF_6:

$$XeF_6 + HF \rightleftharpoons (XeF_5)^+ + HF_2^-$$
$$XeF_6 + 2\,HF \rightleftharpoons (XeF_7)^- + (H_2F)^+$$
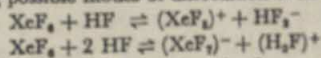
How will you distinguish one from the other?

16.32 The standard oxidation potentials (in volts) in acid and basic solutions for various noble gas species are given below:

$$\textit{In acidic:} \quad Xe(g) \xrightarrow{-2\cdot45} Xe^+ \xrightarrow{-1\cdot67} XeO_3 \xrightarrow{-3\cdot0} H_4XeO_6$$
$$\underrightarrow{\hspace{2em}-2\cdot2\hspace{2em}}$$

$$\textit{In basic:} \quad Xe(g) \xrightarrow{-0\cdot9} HXeO_4^- \xrightarrow{-0\cdot9} [HXeO_6]^{3-}$$
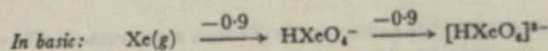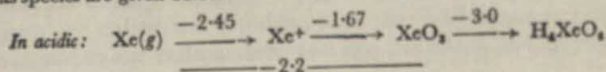
(*i*) Are the species XeO_3, Xe^+, and H_4XeO_6 stable in aqueous solution?

(*ii*) In what solution (acidic or basic) is H_4XeO_6 a more powerful oxidising agent?

(*iii*) What are the species formed when XeO_3 is shaken with dilute acids?

16.33 Why is it unlikely that $XeBr_2$ will be stable?

16.34 Can you explain why xenon (rather than argon or helium) was chosen as the noble gas to be used in the fluorination experiments? Why not radon?

16.35 It is believed that the hydrates of noble gases are similar in structure to the metal alloys of helium. In what way are they similar?

16.36 Would you expect noble gases to form diatomic molecules like N_2 or H_2?

16.37 Why is argon better than nitrogen for filling light bulbs?

17

Chemistry of Transition Elements
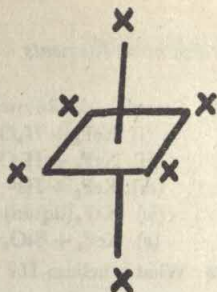
Even when, to judge by the valence number, the combining power of certain atoms is exhausted, they still possess in most cases, the power of participating further in the construction of complex molecules with the formation of very definite linkages. The possibility of this action is to be traced back to the fact that, besides the affinity bonds designated as principal valences, still other bonds called auxiliary valences, may be called into action.

ALFRED WERNER

In the building of the electronic configurations of atoms, electrons are filled in levels of increasing energy in the order $1s$, $2s$, $2p$, $3s$, $3p$, and so on. When we come to the $3d$ and $4s$ levels, certain complications arise in the energy level placings. In multi-electron atoms, the sequence of energy levels not only depends on the electron-nuclear attraction, but also on inter-electron repulsion. Let us consider the $3d$ orbital. The nucleus is shielded by the inner electrons and an electron in the $3d$ orbital experiences an almost constant nuclear attraction until the atomic number, Z, is 20 (calcium). After scandium (atomic number 21) the electron energies of $3d$ shell begin to rise somewhat higher than those of the $4s$ shell. Consequently, the nine elements Sc (Z=21) to Cu (Z=29) fill their $4s$ orbitals first and then the $3d$ orbitals; these elements are referred to as the *first transition series*. On a similar basis, the elements Y (Z=39) to Ag (Z=47), where the progressive filling of the $4d$ levels occurs, are called the *second transition series*, and the elements La (Z=57), and Hf (Z=72) to Au (Z=79) form the $5d$ series or the *third transition series*.

The electronic configurations of these elements are given in Table 3.4. Note that Zn, Cd and Hg have the filled $s^2 d^{10}$ structure; thus these are not regarded as transition elements, but form a group (IIB) by themselves with similar properties. On the same basis, Cu^+, Ag^+ and Au^+ are also not considered to be transition metal ions. Note also that Cr and Mo prefer the d^5 configuration to d^4, and Cu, Ag and Au the d^{10} configuration to d^9; the reason

for this is the greater stability of half- and fully-filled levels.

When we come to atoms with available f orbitals for population, a similar situation is encountered. Since there are seven f orbitals, populating fourteen electrons, one expects similar sets of f series elements, one involving the progressive filling of the $4f$ levels, and another involving the $5f$ levels. The elements cerium $(Z=58)$ to lutetium $(Z=71)$ form the $4f$ series, with the configuration $6s^2 4f^n 5d^0$ (see however Table 3.4 for La, Gd and Lu). These elements, together with La, are called the *lanthanides* or *the rare earths*. They occur together and show similarities in properties such as stable $+3$ oxidation states, less tendency for coordination, similar redox potential values. The gradual filling of the ' inner ' $4f$ shell causes a shrinkage of their (trivalent) ionic radii along the series, which is called the *lanthanide contraction*. This difference in their ionic sizes is used in their separation from the common ore by the *ion-exchange technique*. The $5f$ series of elements from actinium to lawrencium are called the *actinides*, with the configuration $7s^2 5f^n 6d^m$. Many of these elements are radioactive, and are discussed in Chapter 19.

Example 17.1 Do you classify the following ions as transition metal ions? Give reason for your answer: Cu^+, Sc^+, Ti^{4+}, V^{4+}, Cr^+

Cu^+: No, because the $3d$ shell is completely filled.
Sc^+: Yes, because the $3d$ shell has one electron.
Ti^{4+}: No, because the $3d$ shell is completely vacant.
Cr^{3+}: Yes, because the $3d$ shell contains three electrons.

17.1 FIRST TRANSITION SERIES

The elements scandium (atomic number 21) to copper (atomic number 29) are termed the first transition series, where the $3d$ shell is progressively filled $(Sc: 3d^1, \ldots Cu: 3d^{10})$. A study of this series is of interest not only because of the important properties such as complexation, magnetism, colour and variable oxidation states of these elements, but also because these are representative of the other transition series elements.

17.1.1 Occurrence

The elements of the first transition series are relatively abundant in earth's crust. Some of them do not occur in the free state because of their high reactivity and difficulties are encountered in separating them from their ores. The methods chiefly employed for their extraction from the minerals are: electrolysis of the molten halides or their thermal decomposition, and reduction of the oxides formed after roasting the minerals with carbon, carbon monoxide or aluminium. Table 17.1 gives the relative abundance, chief minerals and the chemical reactions involved in the extraction of these elements.

17.1.2 Properties

All these transition elements are hard, malleable, ductile solid metals. They have relatively high densities, high melting and boiling points and high heats of atomisation. These properties indicate that the atoms in these elements are held together by strong metallic bonds that are present in the molten state as well. The strength of such metallic bonding depends upon the interaction

Table 17.1 Abundance, Important Minerals and the Extraction Reaction of the First Transition Series Elements

Element	Electronic configuration	Abundance	Important minerals	Extraction Reaction
Sc	$4s^2 3d^1$	0·0005%	Euxenite; Gadolinite	Ore $\longrightarrow$ $ScCl_3$ $\xrightarrow{\text{Electrolysis in fused state}}$ Sc
Ti	$4s^2 3d^2$	0·6%	Ilmenite ($FeTiO_3$); Rutile (TiO_2)	(1) Ilmenite $\xrightarrow{C + Cl_2 \text{ red heat}}$ $TiCl_4$ $\xrightarrow{\text{reduced with Mg at 800°C}}$ Molten Ti(pure) $\quad$ Ti $\xrightarrow{\text{volatilisation at 100°C}}$ (2) Pure TiI_4 $\xrightarrow{\text{decomposed at high temp.}}$ Ti (Pure)
V	$4s^2 3d^3$	0·2%	Vanadinite ($Pb_5(VO_4)_3Cl$); Carnotite ($KUO_2VO_4,1·5H_2O$)	(1) $V_2O_5 + Ca + CaCl_2$ $\xrightarrow{900°-950°C \text{ in steel bomb}}$ $2\,V + CaO$ (2) Pure VX_4 $\xrightarrow{\text{High temp.}}$ V (pure)
Cr	$4s^2 3d^4$		Chromite ($FeCr_2O_4$)	Chromite + Alkali + O_2 $\xrightarrow{\text{molten state}}$ CrO_4^{2-} $\xrightarrow{\text{Ext}}$ $Na_2Cr_2O_7$ $\xrightarrow[\text{with C}]{\text{reduced}}$ $Cr_2O_3 + Al$ $\xrightarrow[\text{(thermite process)}]{\text{reduced}}$ $Al_2O_3 + Cr$

Element	Electronic configuration	Abundance	Important minerals	Extraction Reaction
Mn	$4s^2 3d^5$	0·085%	Pyrolusite (MnO_2); (Other oxides and carbonates)	(1) $MnO_2 \xrightarrow{heat} 3\,Mn_3O_4 + 8\,Al \xrightarrow[\text{at high temp.}]{\text{reduction}} 9\,Mn + 4\,Al_2O_3$ (2) $MnO_2 + C \xrightarrow{heat} Mn + CO_2$
Fe	$4s^2 3d^6$		Hematite (Fe_2O_3); Magnetite (Fe_3O_4); Limonite (FeOOH); Siderite ($FeCO_3$)	$3\,Fe_2O_3 + CO \xrightarrow{heat} 2\,Fe_3O_4 + CO_2 \xrightarrow{heat}$ $3\,FeO + CO \xrightarrow{heat} Fe$ (pig/wrought iron) Reduction in blast furnace
Co	$4s^2 3d^7$		Smaltite ($CoAs_2$); Cobaltite (CoAsS); Speisses	Ore $\xrightarrow[O_2]{\text{Roast}} MO + SO_2 + As_2O_3$; $MO + $ water gas $\xrightarrow[\text{high temp.}]{\text{Reduce}} Co\,(Ni) \xrightarrow[\text{50°C with CO}]{\text{Heat at}} Ni(CO)_4 + Co$ (Pure) [M represents impure cobalt metal]
Ni	$4s^2 3d^8$		Millerite (NiS); Red nickel (NiAs)	Ore $\longrightarrow Ni_2S_3 \xrightarrow[+\,O_2]{\text{Roast}} NiO + SO_2; NiO \xrightarrow[\text{with C at high temp.}]{\text{Reduced}} Ni$ $Ni(\text{Impure}) + CO \xrightarrow{\text{50°C}} Ni(CO)_4 \xrightarrow[\text{200°C}]{\text{decompose}} Ni$
Cu	$4s^2 3d^9$		Copper pyrites (CuS)	Ore $\xrightarrow[+\,O_2]{\text{Roast}} MO + SO_2; MO + C \xrightarrow[SiO_2\,(\text{flux})]{\text{High temp.}} M + CO, M(\text{Impure}) \longrightarrow$ Electrolysis $\longrightarrow$ pure Cu

between the electrons in the outermost shell. In general, the greater the number of valence electrons available, the stronger is the resultant bonding. Besides, electrons in *d* orbitals form stronger metallic bonds. In the transition metals, a minimum of three electrons $[ns^2 (n-1)d^x]$ are available for interaction with other elements for the metallic-bond formation. Consequently, the bonding in the transition metals is strong. This strong metallic bonding exhibits itself in the properties of the metals. Some of the properties are listed in Table 17.2. The metallic radius of the elements decreases slightly along the series, due to the increase of effective nuclear charge. The metals are, as expected, good conductors of electricity and heat. A number of transition metals occur in more than one crystal form depending upon the thermal history and the presence of an impurity. Thus, iron exists in body centered cubic and tetragonal lattices.

Table 17.2 shows that there is a general increase in the second ionisation energy as the atomic number increases. The exception is manganese.

Example 17.2 Why are the second ionisation energies of chromium and copper larger than those of their neighbouring elements (V, Mn; Ni, Zn)?

The second ionisation energy of Cr and Cu involves the removal of one electron from the 4*s* orbital and another electron from the half-filled and completely filled 3*d*-shell respectively. The half-filled and filled shells have extra stability associated with them and, therefore, the second ionisation energy of these elements are considerably larger than those of the neighbouring elements (see Chapter 3).

Most of the elements of this series or their ions have partially filled *d* orbitals, which is responsible for some interesting magnetic properties. Particular mention must be made of the iron triad elements, iron (core, $3d^6 4s^2$), cobalt (core, $3d^7 4s^2$) and nickel (core, $3d^8 4s^2$), which exhibit *ferromagnetism*. These elements are strongly attracted by magnetic fields and possess permanent magnetisation even in the absence of a magnetic field (see Chapter 7). Most compounds of these as well as other transition elements are paramagnetic and coloured.

17.1.3 Chemical Behaviour

The chemical properties of these elements vary along the series. Each element displays a number of oxidation states. The chemical properties of an element in various oxidation states differ. Thus, the charge to radius ratio, stereochemistry, stoichiometry of compounds and acid-base properties of an element are not only different from those of other transition elements, but also differ from one oxidation state to another of the same element.

The common oxidation states of the elements are given in Table 17.2. The preferred arrangements of the atoms bonded to the elements in their compounds are also given in Table 17.2. Besides these, the elements exhibit several other unusual oxidation states which can be stabilised in complexes with certain ligands.

An examination of the common oxidation states reveals the following correlations:

(*i*) Excepting scandium, the most common oxidation state of these elements is +2 which arises due to the loss of 4*s* electrons; this indicates that, after scandium, *d* orbitals become more stable than the *s* orbitals.

Table 17.2 Properties of the Elements of the First Transition Metal Series

Property		Element								
		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Density, g cc^{-1}		3	4·5	6·0	6·9	7·4	7·9	8·7	8·9	8·9
Melting point, K		1200	1660	1710	1600	1260	1535	1490	1450	1083
Boiling point, K		2730	3260	3450	2660	2150	3000	2900	2730	2600
Atomic radius, A		1·64	1·47	1·35	1·29	1·37	1·26	1·25	1·25	1·28
Ionic radius, A	M^{2+}	—	0·80	0·73	—	0·90	0·85	0·80	0·76	0·69
	M^{3+}	0·69	0·63	0·62	0·62	0·63	0·63	0·56	—	—
Ionisation energy, kcal mol^{-1}	M^{2+}	+446	+470	+493	+536	+532	+554	+576	+594	+646
	M^{3+}	+1018	+1107	+1104	+1274	+1316	+1246	+1359	+1424	+1521
$\Delta H_{hydration}$, kcal mol^{-1}	M^{2+}	—	−453	−464	−468	−454	−480	−497	−516	−516
	M^{3+}	−904	−964	−1010	−1062	−1055	−1027	−1043	—	—
Standard electrode reduction potential, V	$M \rightleftharpoons M^{2+} + 2e$	—	−1·63	−1·2	−0·91	−1·18	−0·44	−0·28	−0·25	+0·34
	$M^{2+} \rightleftharpoons M^{3+} + e$	2·08	−0·37	−0·26	−0·41	+1·51	+0·77	+1·82	+1·68	+2·0
Common oxidation states with preferential geometries (in brackets)[1]		3(O)	2(O) 3(O) 4(T,Tp)	2(O) 3(T,O) 4(T,Tp,O) 5(T,Tp,O)	2(O) 3(c) 6(T)	2(T,P,O) 3(Sp,O) 4(O) 5(T) 6(T) 7(P,T)	2(T,O) 3(T,O)	2(T,O) 3(T,O)	2(P,T,O) 4(O)	1(L,P,T) 2(T,O,P,Tp)

[1]O, octahedral; T, tetrahedral; P, planar; Sp, Square pyramidal; Tp, Trigonal bipyramidal.
For other symbols, refer to Table 16.1.

(*ii*) In the +2 or +3 oxidation states, bonds formed are mostly ionic. The higher oxidation states, usually found in flourine and oxygen containing compounds result from the removal or sharing of d electrons and here the bonds are mostly covalent. For example, in MnO^-_4 all bonds between manganese and oxygen are covalent.

(*iii*) Within a group, the maximum oxidation state increases with the atomic number. Thus, iron shows the oxidation states of +2 and +3, but Os and Ru in the same group form compounds in +4, +6 and +8 oxidation states (OsO_4 is quite stable).

Since the reactivities of the metallic elements and their compounds in the solid state and in solution are different, we shall deal with the chemistry of the transition metals in aqueous solution separately from that in the solid state. Besides, the tendency of the metals to react in the solid state depends upon the particle size and its thermal history. The oxidation of nickel in air is an example of this. A block of nickel does not oxidise in air at ordinary temperatures, while fine nickel powder, freshly obtained through the reduction of NiO by H_2 at 200°C, spontaneously ignites in air. If the same nickel powder is first heated at 400°C in an inert atmosphere, the ignition does not take place even at 300°C.

17.1.4 Reactions in Dry State

All the transition elements react with a number of non-metals, like oxygen, nitrogen, phosphorus, halogens, sulphur and carbon, to form binary compounds. Generally, the reactions take place at elevated temperatures. They also react with other compounds like NH_3, SO_2, HCl, KNO_3, $KHSO_4$ and NaOH at high temperatures.

17.1.5 Oxides

Table 17.3 lists the well-established oxides of the elements of the first transition series, their general methods of preparation, acid-base characteristics, and heats of formation. The general formulae of the oxides are MO, M_2O_3, M_3O_4, MO_2, M_2O_5, and MO_3. In addition to these, titanium and vanadium form homologous series of oxides of the general formula M_nO_{2n-1}. Some interesting electrical, magnetic and other properties of transition metal oxides were examined in Chapter 7.

The oxides having the formula MO have a NaCl-type crystal structure in which each M^{2+} is octahedrally surrounded by six O^{2-} ions and each O^{2-} ion is surrounded by six M^{2+} ions. The trivalent oxides, M_2O_3, have the corundum structure in which each M^{3+} ion is octahedrally surrounded by six O^{2-} ions and each O^{2-} ion is surrounded tetrahedrally by four M^{3+} ions. The dioxides, MO_2, have the rutile structure, while the oxides, M_3O_4 ($MO \cdot M_2O_3$) have the spinel structure (see Chapter 7). V_2O_5 is the only oxide in which the +5 oxidation state is well established. It has a complex layer structure in which vanadium is surrounded by five O^{2-} ions in an irregular way.

All oxides are thermodynamically stable, as shown by their negative heats of formation. Further, oxides of the same metal in different oxidation states have different stabilities and therefore can be partially decomposed or disproportionated on heating. This reaction has been utilised in the preparation of intermediate oxides.

The three oxides of iron, FeO, Fe_2O_3 and Fe_3O_4, form an interesting set to examine. All these three are involved in the metallurgy of iron:

$$3Fe_2O_3 + CO \xrightarrow{200°C} 2\,Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \xrightarrow{350°C} 3\,FeO + CO_2$$

$$FeO + CO \longrightarrow Fe + CO_2$$
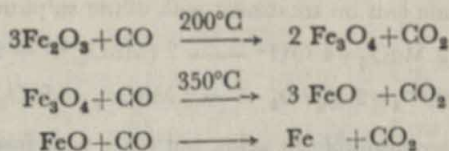
The oxides are basic when the metal is in low oxidation state and acidic in high oxidation state. In the intermediate oxidation state they are amphoteric. They are highly insoluble in water. The basic and amphoteric oxides are dissolved in non-oxidising acids forming hexa-aquo ions, $[M(H_2O)_6]^{n+}$. The rate of dissolution in acid is generally slow unless the oxide is very finely divided. Thus prolonged boiling is necessary to dissolve Cr_2O_3.

The dioxides show a large variation in their chemical behaviour. TiO_2 and MnO_2 are insoluble in water or aqueous acids while VO_2 dissolves in acids to give VO^{2+} ions. MnO_2, which is acidic in character, oxidises hot concentrated

Table 17.3 Methods of Preparation, Heats of Formations (in kcal mol^{-1}), and Acid-Base Character of Transition Metal Oxides

---

Sc $b, 3, 5$ $[Sc_2O_3]$ (-411)

Ti $b, 1$ $[TiO]$ (-124); $c, 1$ $[Ti_2O_3]$ (-363); $c, 3, 5$ $[TiO_2]$ (-225)

V $b, 1$ $[VO]$ (-100); $b, 2$ $[V_2O_3]$ (-296); $c, 7$ $[VO_2]$ (-171); $a, 5$ $[V_2O_5]$ (-373)

Cr $b, 3$ $[Cr_2O_3]$ (-273); $a, 8$ $[CrO_2]$ (-142); $a, 5$ $[CrO_3]$ (-138)

Mn $b, 2, 3$ $[MnO]$ (-92); $c, 6$ $[Mn_2O_3]$ (-229); $c, 6$ $[Mn_3O_4]$ (-331); $a, 5$ $[MnO]$ (-124)

Fe $b, 4$ $[FeO]$ (-64); $c, 3, 5$ $[Fe_2O_3]$ (-197); $b, 6$ $[Fe_3O_4]$ (-268)

Co $b, 3$ $[CoO]$ (-57); $a, 8$ $[CoO_2]$ (-204)

Ni $b, 5$ $[NiO]$ (-57)

Cu $b, 6$ $[Cu_2O]$ (-40); $b, 5$ $[CuO]$ (-38)

---

a, acidic;   *b*, basic;   *c*, amphoteric

1: Reduction of higher oxides by the metal; 2: Reduction of higher oxides by H_2 or CO; 3: Pyrolysis of metal hydroxide or carbonate; 4: Pyrolysis of metal oxalate; 5: $M + O_2 \rightarrow M$ oxide; 6: Pyrolysis of metal oxide; 7: Heating of lower and higher oxides together; 8: $MO + O_2 \rightarrow MO_x$. Number in parenthesis indicates the heats of formation.

HCl forming chlorine gas and $Mn^{2+}(aq)$. With fused alkali, MnO_2 produces *manganate* in the presence of KNO_3 or oxygen; these MnO^{2-}_4 are oxidised to permanganate ions on treatment with dilute sulphuric acid:

$$2\ MnO_2 + 4\ OH^- \longrightarrow 2\ (MnO_4)^{2-} + 2\ H_2O;$$

$$3\ MnO^{2-}_4 + 2\ H_2SO_4' \longrightarrow 2\ MnO^-_4 + MnO_2 + 2\ SO^{2-}_4 + 2\ H_2O$$
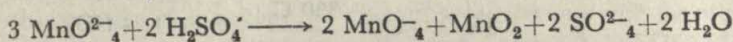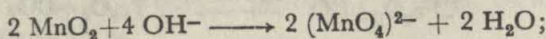
M_3O_4 oxides are insoluble in acids, but react with fused $KHSO_4$ to give the sulphates.

$$2\ Fe_3O_4 + 18KHSO_4 + \tfrac{3}{2}O_2 \longrightarrow 3Fe_2(SO_4)_3 + 9K_2SO_4 + 9H_2O$$

Chromium trioxide, unlike other oxides, is soluble in water forming di-chromate ions: $2\ CrO_3 + H_2O \longrightarrow H_2Cr_2O_7$. It is a powerful oxidising agent particularly towards organic compounds, the decomposition occurring step-wise in many stages: $CrO_3 \longrightarrow Cr_3O_8 \longrightarrow Cr_2O_5 \longrightarrow CrO_2 \longrightarrow Cr_2O_3$. When it reacts with alkali it forms chromate:

$$CrO_3 + 2\ OH^- \longrightarrow CrO^{2-}_4 + H_2O$$
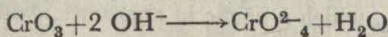
The structures of the chromate and dichromate ions are shown in Fig. 17.1.

All the oxides can be reduced by carbon or aluminium, usually at high temperature. Hydrogen reduces the oxides of these elements which are low in the electrochemical series, but the reduction does not take place in those cases where metals are higher-up in the series. Thus, Cr_2O_3 cannot be reduced while CuO can be reduced by hydrogen. The reduction of metal oxides using aluminium forms the basis of the thermite process used in

Fig. 17.1 Structures of (a) chromate and (b) dichromate ions

the extraction of metals. Copper is the only metal that forms an oxide in its +1 state. Copper also forms a +3 state oxide, which is unstable.

17.1.6 Halides

Transition elements react with halogens to give various halides. Generally, one needs to heat the reactants in order to initiate the reaction owing to the high activation energy. But once the reaction starts, the heat of reaction is sufficient to continue it. The order of reactivity of the halogens is, $F > Cl > Br > I$. Metals are usually oxidised to a higher oxidation state with fluorine than with chlorine or any other halogen, due to the greater oxidising power of fluorine compared to other halogens.

Fluorides are prepared (i) by the direct combination of fluorine with metals or (ii) by the reaction of hydrogen fluoride on metals, metal oxides or halides. The first method is used to prepare the fluorides in which the metal ions are in higher oxidation states (e.g. TiF_4, CuF_2, FeF_3). The second method is used to get those fluorides in which the metals are in lower oxidation state (e.g. TiF_3). Chlorides, bromides and iodides of transition metals having higher oxidation state are prepared either by the action of respective halogens on a heated mixture of oxide and carbon or by the direct combination of metals and halo-gens. The chlorides, bromides and iodides of metals in lower oxidation state

are prepared either by the reduction of higher halides with respective metals or by their thermal decomposition. The halides are known to hydrolyse with ease.

$$FeCl_2 \cdot H_2O \rightarrow Fe(OH)Cl + HCl$$
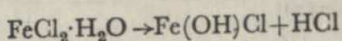
Halides of metals in higher oxidation states have a great tendency to hydrolyse and are less stable. Thus, $TiCl_4$ hydrolyses to give TiO_2 and HCl ($TiCl_4 + 2 H_2O \rightarrow TiO_2 + 4$ HCl). They can be decomposed on heating to form free halogen and halides in which the metal ions are in lower oxidation states.

The bonding in fluorides is mostly ionic. In chlorides, bromides and iodides the ionic character of metal to halogen bond goes on decreasing with the atomic mass of halogen. Thus, the iodine-metal bond has a large covalent character. For example, CuF_2 is an ionic solid with the fluorite structure while anhydrous $CuCl_2$ and $CuBr_2$ consist of infinite chains of atoms due to covalent bonding (Fig. 17.2).
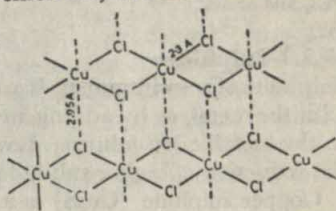
Fig. 17.2 Polymeric structure of cupric chloride

As opposed to oxides, the halides have a lesser tendency to deviate from the octahedral symmetry. The exception is CuX which has the ZnS structure (4:4 coordination) due to its high covalency. The difluorides of Cr, Mn, Fe, Co, and Ni have rutile structure: $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$ are cubic closed packed and MnI_2, $FeBr_2$, FeI_2, $CoBr_2$, CoI_2, $NiBr_2$ have hexagonal closed packed structures in which one third octahedral holes are filled with metal ions. $CrBr_3$, $FeCl_3$, $FeBr_3$ have hexagonal closed packed and $CrCl_3$ cubic closed packed structures.

Example 17.3 Write equations for the various reactions given below: A bottle of titanium tetrachloride, when opened gave a white smoke. The contents of the bottle, when added to concentrated hydrochloric acid, gave a colourless solution of a complex ion. When zinc metal was added to this, a violet coloured solution was produced. To this violet coloured solution, aqueous alkali was added slowly until the solution became alkaline. A purple coloured solid precipitated out, which was removed by filtration and treated with nitric acid followed by dilute aqueous alkali. A white solid resulted which on fusion with an equimolar quantity of magnesium oxide gave a complex oxide.

(i) $TiCl_4 + 2 H_2O \rightarrow TiO_2 + 4$ HCl (SMOKE REACTION)

(ii) $TiCl_4 + 2 Cl^- \rightarrow (TiCl_6)^{2-}$ (COMPLEX ION IN HCl SOLUTION)

(iii) $2(TiCl_6)^{2-} + Zn + 2 m H_2O \rightarrow$
$Zn^{2+} + 2[Ti(H_2O)_mCl_{6-m}]^{(m-3)+} + 2 m Cl^-$

(iv) $2 Ti^{3+} + 5 OH^- \xrightarrow{H_2O} [Ti_2O_3 \cdot 3H_2O]$ (PINK SOLID)

(v) $2[Ti_2O_3 \cdot 3H_2O] + 2 HNO_3 \rightarrow 4TiO_2 + 7H_2O + NO + NO_2$ (OVERALL)

(vi) $TiO_2 + MgO \rightarrow Mg TiO_3$ (COMPLEX OXIDE—ILMENITE)

Example 17.4 Comment on the following observations: (i) CCl_4 vapours react with red hot vanadium (V) oxide* to give vanadium (IV) chloride. (ii) Vanadium (III) chloride forms vanadium (IV) chloride on heating in excess of chlorine and vanadium (II) chloride on heating in vacuum.

*The roman numerals in parentheses after the element denote the oxidation state of the atom.

General Chemistry

(i) This is a general method of preparation of transition metal halides. Vanadium (V) halide is not stable.

(ii) Two equilibria are involved in this:

   (a) $2VCl_3 \rightleftharpoons VCl_2 + VCl_4$

   (b) $VCl_4 \rightleftharpoons VCl_3 + \frac{1}{2} Cl_2$

Thus, with an excess of chlorine, equilibrium (b) is driven towards the left forming VCl_4. But, when chlorine is pumped away, equilibrium (b) shifts to the right forming VCl_3 which disproportionates into VCl_2 and VCl_4 according to equation (a). VCl_4, thus formed again gives VCl_3 and so on.

17.1.7 Sulphides

Sulphides of transition metals are prepared either by the direct union of sulphur with the metal, or by adding any sulphide forming compound like H_2S or Na_2S to the metallic ion solution. Lower sulphides like Cu_2S or VS are prepared by the reduction of higher sulphides (or halides) with sulphur.

Copper sulphide (Cu_2S) is a non-stoichiometric sulphide, and is normally deficient in copper, approximating to the formula, Cu_9S_5. Since sulphur is not a powerful oxidising agent, sulphides are generally formed with the metals in their lower oxidation states. Transition metal sulphides are highly coloured or black. They are macromolecular and insoluble in water, with heats of formation lower than those of oxides (and therefore less stable). When treated with oxidising acids, sulphur is precipitated out; in some cases, the sulphide is oxidised to sulphate. Higher sulphides are hydrolysed by water with the formation of hydrogen sulphide and hydrated oxides. Iron pyrites (FeS_2) is an interesting sulphide which is nonstoichiometric.*

17.1.8 Hydrides

Nearly all the transition metals *adsorb* (capture at surface) hydrogen. The M—H bond cannot be classified either as covalent or ionic. These hydrides are of variable composition (e.g. TiH_x). In some cases, hydrogen is adsorbed on the metal surface where hydrogen molecules are dissociated into atoms. The atoms then diffuse into the bulk of the solid and occupy the empty spaces (interstitial space) between the atoms of the metal. Such hydrides are classified as interstitial hydrides.

17.1.9 Reaction with Carbon, Boron and Nitrogen

At high temperatures, transition metals interact with carbon, boron, and nitrogen. In these compounds small atoms of carbon, boron and nitrogen can occupy the empty spaces of the transition elements to form interstitial compounds called carbides, borides and nitrides respectively. The spaces in the metal crystals of Cr, Mn, Fe, Co and Ni are not large enough to accommodate carbon atoms. These carbon atoms cause a distortion in the metal lattice and therefore these carbides are highly reactive. In some cases, the presence of foreign atoms stabilises the metal lattice with the result these interstitial compounds are high-melting, hard and inert and retain their metallic conductivities. Such compounds are used in kilns, gas turbines, jet engines, heat resistant materials and for cutting tools.

*Its crystal structure can be described in terms of the NaCl structure. In this structure S^{2-} are discrete and occupy the position of Cl^- in NaCl structure and Fe^{2+} occupy the position of Na^+.

17.1.10 Chemistry in Aqueous Solution

The chemistry of any element in solution is determined mainly by the redox potential of the element and its tendency to form complex ions in solution. Scandium has a standard reduction potential (Sc^{3+}, Sc) of -2.08 V and is thus a strong electropositive element; it is oxidised by H^+ to Sc^{3+} and H^+ itself is reduced to hydrogen gas.* In this way, scandium resembles the elements of group IIIA. In basic medium, scandium ions precipitate as $Sc(OH)_3$ or $Sc_2O_3 \cdot x\ H_2O$. In acid and neutral media, the complex ion, hexa-aquo scandium (III) ion, $[Sc(H_2O)_6]^{3+}$ is obtained.

Titanium in its zero or $+2$ oxidation state $(E^\circ_{red}: Ti^{2+}, Ti = -1.63$ V, $E^\circ_{red}: Ti^{3+}, Ti^{2+} = -0.37$ V) is a good reducing agent, reducing H^+ in neutral and acid solutions with the formation of the thermodynamically more stable species, $[Ti(H_2O)_6]^{3+}$. Thus, Ti^{2+} state is of no importance in aqueous medium. Ti^{4+} has a large charge density (charge to radius ratio), and in aqueous solution $[Ti(H_2O)_6]^{4+}$ is extensively hydrolysed to $[Ti(H_2O)_3(OH)_3]^+$. The trivalent ion, $[Ti(H_2O)_6]^{3+}$ is also not stable in air or oxygen, and is oxidised to the hydroxo-species of Ti^{4+}.

Similar to titanium, vanadium metal is a strong reducing agent $(E^\circ_{red}: V^{2+}, V = -1.2$ V) and V^{2+} is a moderately good reducing agent. The ion V^{2+} is also not very stable in aqueous solution and in the presence of air or oxygen gets oxidised to V^{3+} $(E^\circ_{red}: V^{3+}, V^{2+} = -0.26$ V). Turning to higher oxidation states, $V(V)$ is reduced by Zn or Fe^{2+} in acid, whereby a blue solution of vanadium (IV), the VO^{2+}, (*vanadyl* ion) results. Vanadium (IV) is amphoteric, when treated with alkali, VO_2 precipitates which on treating with a strong base dissolves to form the ion, VO_4^{4-}, and its polymerised products. Vanadium pentoxide, V_2O_5, dissolves in acid to form the *pervanadyl* ion, (VO_2^+), and its polymerisation products:

$$V_2O_5 + 2\ H^+\ (aq) \rightarrow 2\ VO_2^+ + H_2O$$
$$10(VO_2)^+ + 8H_2O \rightarrow (H_2V_{10}O_{28})^{4-} + 14\ H^+$$
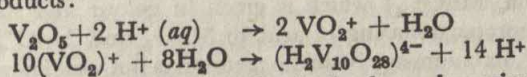
In basic solution, V_2O_5 dissolves as VO_4^{3-} which also polymerises to $(V_3O_9)^{3-}$ and other species:

$$V_2O_5 + 3OH^- \rightarrow 2VO_4^{3-} + 3H^+; \qquad 3\ VO_4^{3-} + 6H^+ \rightarrow V_3O_9^{3-} + 3H_2O$$
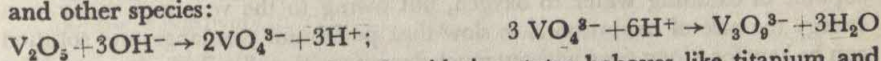
Chromium in its zero and $+2$ oxidation states behaves like titanium and vanadium. If we compare the oxidation potential of Cr^{+3} with those of other the transition metal ions $(Ti^{3+}, V^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Cu^{3+})$, we see that the elements before chromium are good reducing agents and the elements after chromium $(Mn^{3+}, Fe^{3+}, Co^{3+}, Cu^{3+})$ are strong oxidising agents. In aqueous solution, Cr^{3+} exists as $[Cr(H_2O)_6]^{3+}$ ion which is slightly hydrolysed to $[Cr(H_2O)_5(OH)]^{2+}$. In basic medium, extensive hydrolysis occurs and $Cr(OH)_3$ precipitates out. Addition of $(NH_4)_2S$ or Na_2CO_3 to an acid or neutral solution of Cr^{3+} precipitates it as $Cr(OH)_3$. In alkaline solutions chromium (III) is oxidised to chromium (IV) (*chromate*):

$$Cr(OH)_3 + 5(OH)^- \rightarrow CrO_4^{2-} + 4H_2O + 3\ e \qquad (E^\circ_{red} = -0.13V)$$
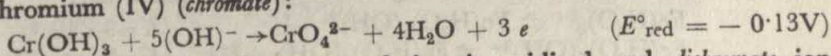
On acidification, the chromate solution is oxidised and *dichromate* ion $Cr_2O^{2-}_7$, is formed. Thus, in the neutral medium, there is an equilibrium between dichromate and chromate ions:

$$2\ CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$
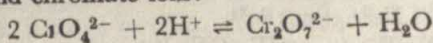
*We shall use throughout the convention employed in Chapter 12 for standard reduction potentials.

Comparison of the reduction potentials of the O_2/O^{2-} couple with Cr^{6+}/Cr^{3+} couple shows that the dichromate ion solution is unstable with respect to decomposition to oxygen and chromium (III). The rate of decomposition is very slow and the dichromate solution can be kept for a very long time without any sign of reduction. The dichromate ion can be dehydrated with concentrated sulphuric acid to form an oxide (CrO_3) which is a very powerful oxidising agent.* Chromous ion, Cr(II) can be prepared by the reduction of chromium (III) with zinc.

Manganese metal is electropositive and forms manganese (II) in acid solution. This behaviour is identical with other transition metals. But it differs from doubly charged ions of titanium, vanadium and chromium in having no reducing properties. In fact, it is difficult to oxidise Mn^{2+} to Mn^{3+} in aqueous solution $Mn^{3+},/(Mn^{2+}$ $E°_{red}=+1.51$ V). In basic medium, Mn^{2+} is precipitated as $Mn(OH)_2$ which can be easily oxidised to $MnO_2(E°_{red}= -0.05$ V).

The ion Mn^{3+} does not exist in aqueous solution and disproportionates into Mn^{2+} and MnO_2. This is shown by the combination of the following half reactions:

$$Mn^{3+} + e \rightleftharpoons Mn^{2+} \qquad\qquad E° = 1.51 \text{ V}$$
$$MnO_2 + 4 H^+ + e \rightleftharpoons Mn^{3+} + 2 H_2O \qquad\qquad E° = 0.95 \text{ V}$$

$$\overline{2 Mn^{3+} + 2 H_2O \rightleftharpoons Mn^{2+} + MnO + 4 H^+ \qquad E° = 0.56 \text{ V}}$$
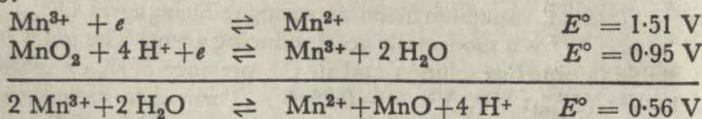
Consequently, there is no aqueous chemistry of manganese (III). In acid solution, MnO_2 is a powerful oxidising agent and is reduced to Mn^{2+}. Thus, MnO_2 will oxidise HCl to form Cl_2 gas and Mn^{2+}, while in basic solution, it is quite stable as shown by its redox potential.

Manganese dioxide can be oxidised in basic media to manganese (VI), (*manganate* ion, MnO^{2-}_4) which is green in colour and stable only in basic medium, disproportionating in acid to MnO_2 and MnO^-_4. Thus, owing to its instability, its chemistry in acidic medium is not well known.

Manganese in the +7 oxidation state is a powerful oxidising agent. It is capable of oxidising water to oxygen, but owing to the very high activation energy the rate of oxidation is so slow that potassium permanganate solution can be kept for a long time without much decomposition. Similarly, it can oxidise HCl to chlorine, but again at room temperature, the rate of oxidation is very slow. Due to its powerful oxidising power, Mn^{7+} (MnO^-_4 ions) is formed only by the oxidation of Mn^{2+} with a very powerful oxidising agent such as sodium bismuthate.

The next two elements, iron and cobalt, occur commonly in their +2 and +3 oxidation states. Co(III) is much more powerful as an oxidising agent than Fe^{3+}. Its reduction potential shows that Co^{3+} cannot exist in aqueous solution and oxidises water to oxygen. Fe^{3+}, because of its large charge and small size, hydrolyses or acts as an acid according to the following equilibrium:

$$Fe(H_2O)_6^{3+} \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H^+ \qquad (K=9 \times 10^{-4})$$
$$Fe(H_2O)_5(OH)^{2+} \rightleftharpoons Fe(H_2O)_4(OH)_2 + H^+ \qquad (K=5.5 \times 10^{-4})$$
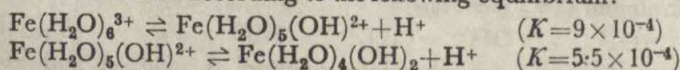
The relative stabilities of any redox couple can be affected by the formation of complex ion formation. Thus,

$$Fe^{3+} + e \rightleftharpoons Fe^{2+} \qquad\qquad E°=0.771 \text{ V}$$
$$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-} \qquad\qquad E°=0.36 \text{ V}$$
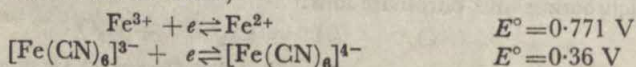
*This oxide is used to oxidise grease and other organic matter in cleaning chemical glassware.

Thus an unstable ion can be stabilised by complexing it with a suitable complexing agent. The ion Co^{3+} which decomposes water to oxygen, can be stabilised by complexing it with NH_3, CN and such *ligands*.

In aqueous or acid solution, nickel exists as green ion, $[Ni(H_2O)_6]^{2+}$, and in base $Ni(OH)_2$ precipitates out. It can be oxidised in basic medium to NiO_2, but in acid medium Ni^{4+} is not stable and oxidises water to oxygen. Copper is the only element which exists in the $+1$ oxidation state. However, in this state it is not stable and disproportionates into copper metal and Cu^{2+}. The ions Cu^{2+} exist as blue $[Cu(H_2O)_5]^{2+}$ in acid or neutral medium and precipitate as $Cu(OH)_2$ in basic media.

17.2 SECOND AND THIRD TRANSITION SERIES

The elements of the second and the third transition series have not been as extensively studied as those of the first transition series. The chemistry of the second and third series elements, while quite similar to the $3d$ group, shows differences from them due to differences in electronic configurations.

17.2.1 Occurrence
Most of these elements are rare and present as minor constituents in the ores of other elements. Therefore, they are extracted from the sludges of other ores. Their principal sources and the general methods of extractions are given in Table 17.4. Similar to the first transition series elements, the second and third transition series elements exhibit metallic behaviour. They have high densities, high melting and boiling points, high heats of sublimation, and are good conductors of heat and electricity. Quite a number of them occur in more than one crystal form. Some of these properties are shown in Table 17.4. We see that the densities and melting points of these elements are greater than those of the first series elements. The combination of high stability of solids (as shown by their melting points) and higher ionisation energies of the platinum metals make them relatively inert.

17.2.2 Chemical Behaviour
These elements exhibit great variation in their chemical properties. Similar to the first transition series elements, they show a number of different oxidation states, higher oxidation states being more prevalent in the second and third series of elements. The elements of the second and the third transition series undergo disproportionation in the $+2$ oxidation state. Also, the ionisation energies of the elements of the second and the third series are much lower than those of the corresponding members of the first series. Thus, it is easier to ionise the electrons in the $4d$- and $5d$-orbitals than those in the $3d$ orbital (a common trend down a group).

17.3 COORDINATION COMPOUNDS

Many metal ions behave as Lewis acids and accept electron pairs from different types of Lewis bases. We saw in Chapter 11 that an ion like Na^+ interacts with water molecules via ion-dipole forces and exists in aqueous solutions as $[Na(H_2O)_6]^+$ ions. This is an example of *coordination* where the Lewis base H_2O

Table 17.4 Properties of Elements of the Second and Third Transition Series

Element	Atomic Number	Outer electronic configuration	Density g cc⁻¹	Melting point °C	ΔH sublim kcal mol⁻¹	Oxidation states	Occurrence
				SECOND TRANSITION SERIES			
Yttrium, Y	39	$4d^1 5s^2$	5·5	1490	—	3	Zircon (ZrSO₄)
Zirconium, Zr	40	$4d^2 5s^2$	6·4	1860	146	2,3,4	Niobite (Fe(NbO₂)₂)
Niobium, Nb	41	$4d^4 5s^1$	8·6	1950	173	3,5	Molybdenite (MoS₂)
Molybdenum, Mo	42	$4d^5 5s^1$	10·2	2620	157	2,3,4,5,6	
Technetium, Tc	43	$4d^5 5s^1$	11·5	2100	155	2,4,6,7	in Pt ores
Ruthenium, Ru	44	$4d^7 5s^1$	12·4	2450	144	3,4,6,8	Impurity in Pt, Pd ores
Rhodium, Rh	45	$4d^8 5s^1$	12·4	1970	133	3,6	Braggite (Pt, PdS)
Palladium Pd	46	$4d^{10} 5s^0$	12·0	1550	91	2,4	Argentite (Ag₂S), Horn silver (AgCl)
Silver, Ag	47	$4d^{10} 5s^1$	10·5	961	68	1,2	
				THIRD TRANSITION SERIES			
Lanthanum, La	57	$5d^1 6s^2$	—	—	—	3,4	Minor amounts in Zr Ores
Hafnium, Hf	72	$5d^2 6s^2$	13·3	2200	168	4,5	Tantalite, Fe(TaO₃)₂
Tantalum, Ta	73	$5d^3 6s^2$	16·6	3000	186	2,3,4,5,6	Wolframite, FeWO₄
Tungsten, W	74	$5d^4 6s^2$	19·3	3370	200	3,4,5,6,7	as impurity in MoS₂
Rhenium, Re	75	$5d^5 6s^2$	20·5	3200	186	3,4,6,8	as impurity in Pt, Pd ores
Osmium, Os	76	$5d^6 6s^2$	22·7	2700	165	3,4,6	as impurity in Pt, Pd ores
Iridium, Ir	77	$5d^7 6s^2$	22·6	2450	155	2,4,6	Braggite, spherylite, PtS
Platinum, Pt	78	$5d^9 6s^1$	21·5	1774	135	1,3	Gold metal; also in pyrites
Gold, Au	79	$5d^{10} 6s^1$	19·3	1063	87		

(termed the *ligand,* from the Greek word *ligare* to bind) surrounds the central metal ion, to form a *complex ion.* Depending on the size, electronic configuration and the charge on the metal ion, the number of ligands surrounding it (coordination number) and their spatial arrangements would vary. By and large, the same arguments used in Chapter 7 on the types and geometry of coordination apply here also. When we turn to the transition metals, however, the nature of coordination changes somewhat. There are unfilled $3d$ levels, and also the energy differences between $3d$-, $4s$-, and $4p$-levels are small. This offers the possibility of hybridisation of orbitals, variety of oxidation states and thus a variety of ligand-binding possibilities, with forces greater than the ion-dipole forces.

The first systematic study of coordination compounds was done by Alfred Werner almost a century ago. Werner prepared a number of coloured coordination complexes of the $3d$ transition metal ions such as Fe^{2+}, Co^{2+}, Co^{3+}, Ni^{2+} and so on. Cobalt (III) chloride complexes with ammonia to give a beautiful coloured compound of the formula $CoCl_3 \cdot 6NH_3$. Table 17.5 lists some complex compounds of Co(III).

Table 17.5 Complex Compounds of Cobalt (III)

Formula	Structure	Colour	Number of ions
$CoCl_3 \cdot 6NH_3$	$[Co(NH_3)_6]^{3+}\ 3Cl^-$	Orange	4
$CoCl_3 \cdot 5NH_3 \cdot H_2O$	$[Co(NH_3)_5(H_2O)]^{3+}\ 3Cl^-$	Rose	4
$CoCl_3 \cdot 5NH_3$	$[Co(NH_3)_5Cl]^{2+}\ 2Cl^-$	Purple	3
$CoCl_3 \cdot 4NH_3$	$[Co(NH_3)_4Cl_2]^+\ Cl^-$	Green	2
$CoCl_3 \cdot 3NH_3$	$[Co(NH_3)_3Cl_3]$	Blue-green	0

Coordination compounds occur widely in nature. The group that is responsible for the red colour of blood is the heme group, a coordination complex of iron; the green colour of plants is due to the presence of chlorophyll, a magnesium complex; and vitamin B_{12} is a coordination compound of cobalt (see Chapter 18 for some structures). In these compounds, as in many others, the ligands may offer more than one site (groups with electron pairs) that can coordinate to the central metal ion. Such ligands with multiple attachment sites are referred to as *multidentate* ligands. Complexes involving multidentate ligands are
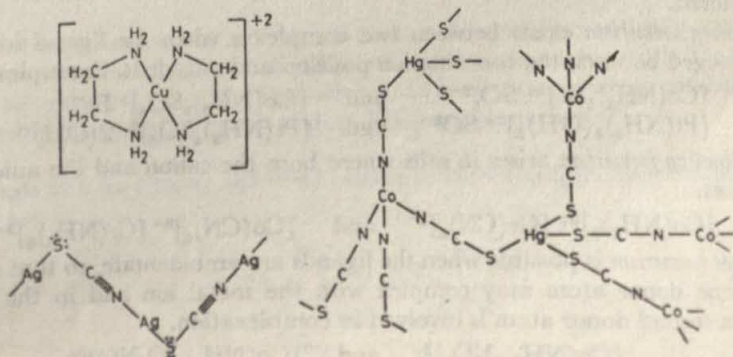
also called *chelates* (derived from the Greek word that refers to the grasp by a crab using its claws). The ligand *ethylene diamine*, $NH_2—CH_2—CH_2—NH_2$, chelates with copper (II) at two positions to yield the chelate complex *bis-(ethylene diamine) Cu(II) ion* (page 593).

There are other ligands that possess two different groups (potential donors), each of which can coordinate to a metal atom. An example is the ion SCN^-. This ion, being linear, will not chelate, but may use either S or N atom, or both (*ambidentate*) to complex with metals (see page 593 for an example). And there are yet others that behave as *bridging* ligands, as in AgSCN (page 593) or Al_2Cl_6 (structure given in Chapter 16).

17.3.1 Isomerism in Coordination Compounds

The first attempt at an explanation of the bonding features and the isomerism of coordination compound was by Werner, who proposed that there are two kinds of valence present in these systems: *principal bonding forces* and *secondary valence forces*. The ionic bond and the bonding in the ligand itself are the principal bonds, while the interaction between the metal and the ligand is termed the secondary valence force. Even after the principal valences are satisfied, the metal still possesses secondary attractions towards the ligands, and complexes them around itself. Werner further visualised that the ligands are arranged in specific orientations in space around the central metal ion as polyhedra. Some examples are given below:
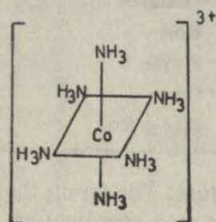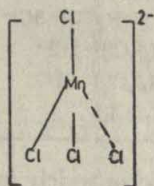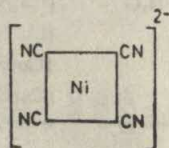
Octahedral coordi-   Tetrahedral coordi-   Square-planar
nation $[Co(NH_3)_6]^{3+}$ nation $[MnCl_4]^-$ coordination $[Ni(CN)_4]^{2-}$

This three-dimensional picture of transition metal complexes gives rise to the possibility of isomerism in these compounds, a fact realised by Werner.

Several of the isomeric possibilities discussed in Chapter 5 are also seen in coordination compounds. The following are the different types generally encountered.

Ionisation isomerism exists between two complexes when the ligand ions are interchanged between the coordination position and outside it. Examples are:

$[Co(NH_3)_5Br]^{2+} SO_4^{2-}$ and $[Co(NH_3)_5SO_4]^+ Br^-$
$[Pt(NH_3)_4(OH)_2]^{2+} SO^{2-}_4$ and $[Pt(NH_3)_4SO_4]^{2+} 2(OH)^-$
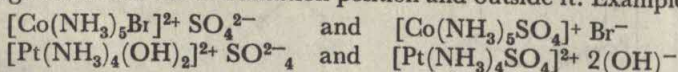
Coordination isomerism arises in salts where both the cation and the anion are complexes.

$[Co(NH_3)_6]^{3+} [Cr(CN)_6]^{3-}$ and $[Co(CN)_6]^{3-} [Cr(NH_3)_6]^{3+}$
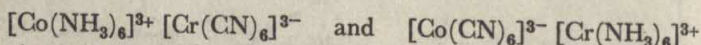
Linkage isomerism is possible when the ligands are ambidentate, so that in one isomer one donor atom may complex with the metal ion and in the other isomer, a second donor atom is involved in complexation.

$[Co(NH_3)_5NO_2]^{2+}$ and $[Co(NH_3)_5 O-NO]^{2+}$
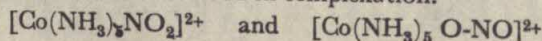
Ligand isomerism is obtained when a central metal ion complexes with a ligand which itself possesses isomeric possibilities, e.g.

[Co (1, 2-DIAMINOPROPANE)$_2$ Cl$_2$]$^+$ and [Co (1, 3-DIAMINOPROPANE)$_2$ Cl$_2$]$^+$
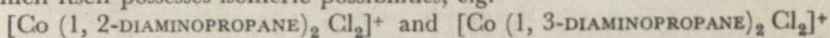
Stereoisomerism arises due to different spatial arrangement of ligands in the complex. If we consider a planar complex of the type Pt(NH$_3$)$_2$Cl$_2$, both the *cis*- and *trans*-geometry are possible:
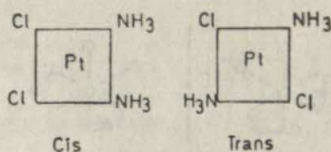
In an octahedral complex, we have:
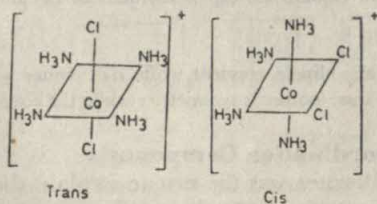
Optical isomers are those which are not superimposable on their mirror images (Chapter 5). Such isomers arise in a molecule that does not possess either a centre- or a plane -of-symmetry. We may visualise now how such possibilities arise in complex compounds also. If we consider the chelate complex *tris-*(*ethylene diamine*) Co(III) *ion*, abbreviated as [Co(en)$_3$]$^{3+}$, two stereoisomers result, where each bidentate ligand is arranged alternatively. The two forms
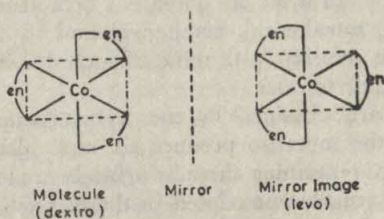
are not superimposable on each other and thus will be optically active. The *d*-isomer rotates the plane of polarised light to the right, while the *l*-isomer does so to the left (Chapter 5). Such optical isomerism occurs in octahedral and in tetrahedral complexes but seldom in square planar ones.

Example 17.5 Show the *cis*- and *trans*-isomerism in Co(NH$_3$)$_4$Cl$_2$ [dichlorotetrammine cobalt (III)] ion.
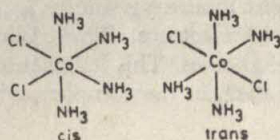
Example 17.6 Give the geometrical and optical isomers of dichlorobis (ethylenediamine) cobalt (III) ion.

trans–isomer

cis   mirror   cis
optical isomers
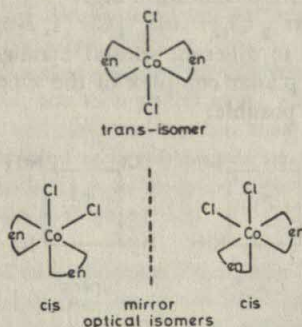
Example 17.7 How can you explain the dipole moment of *cis-* and *trans*-isomers of square-planar $Pt(NH_3)_2Cl_2$?

Trans-isomer will not have any dipole moment while *cis*- isomer will have a finite value of dipole moment, because the *trans*-isomer is symmetric, while the *cis* is not.

17.3.2 Bonding in Coordination Compounds

As mentioned earlier, Werner was the first to explain the bonding features in complexes. He used the term 'secondary valence' to explain coordination. Such an idea proved useful in explaining the structure, ionic nature, and isomerism in these compounds. With the advent of modern theories of valence, it is possible now to discuss the bonding scheme in complexes in terms of various theories, and explain many properties of these compounds such as colour, geometry, magnetic properties and so on.

In the valence bond scheme, 3*d*-, 4*s*- and 4*p*-orbitals of the metal are first hybridised together to yield a set of equivalent orbitals of definite geometry, such as square planar, tetrahedral, octahedral and so on. These hybridised orbitals are allowed to overlap with those of such donor atoms of the ligand that have an electron pair to offer.

Octahedral complexes are obtained by the hybridisation of the metal 3*d*-, 4*s*- and 4*p*-orbitals of the metal to produce six equivalent hybrid orbitals of d^2sp^3 hybridisation. The remaining three 3*d* orbitals are left unhybridised, and the metal 3*d* electrons are accommodated in these. Each ligand in the *X*-, *Y*- or *Z*-direction is allowed to bond to these hybrid orbitals so as to give an octahedral complex, made up of a σ bond between each ligand and the metal. This can be illustrated by means of the schematic box diagram shown in Fig. 17.3. Cr^{3+} has a $3d^3$ configuration, and forms the octahedral complex $[Cr(NH_3)_6]^{3+}$. σ bonds are formed between each NH_3 (electrons in the sp^3 orbital of nitrogen) and the hybrid $d^2 sp^3$ orbital of Cr^{3+}. The three 3*d* electrons of Cr^{3+} are placed in the unhybridised d_{xy}, d_{yz} and d_{xz} orbitals. An interesting outcome of this scheme is that if there are unpaired electrons in the molecule, it should behave paramagnetic with a magnetic moment given by $\mu = n(n+2)$ magnetons where n is the number of unpaired electrons. Thus $[Cr(NH_3)_6]^{3+}$ will exhibit a magnetic moment of 3·9 magnetons. This is because the three 3*d* electrons of Cr^{3+} occupy one 3*d* orbital each in the complex, in accordance with Hund's rule (Chapter 3).

Metal orbitals in the free ion   Metal orbitals in the complexed species

Cr^{3+}

$3d_{xy}$ yz zx x^2-y^2 z^2 4s 4px 4py 4pz $3d_{xy}$ yz zx d^2sp^3 hybrids

Octahedral $\left[Cr(NH_3)_6\right]^3$

V^{3+}

$3d_{xy}$ yz zx x^2-y^2 z^2 4s 4px 4py 4pz   3d yz zx d^2sp^3 hybrids

Octahedral $\left[V(H_2O)_6\right]^{3+}$

Fe^{3+}

$3d_{xy}$ yz zx x^2-y^2 z^2 4s 4px 4py 4pz $3d_{xy}$ yz zx d^2sp^3 hybrids

Octahedral $\left[Fe(CN)_6\right]^{3-}$
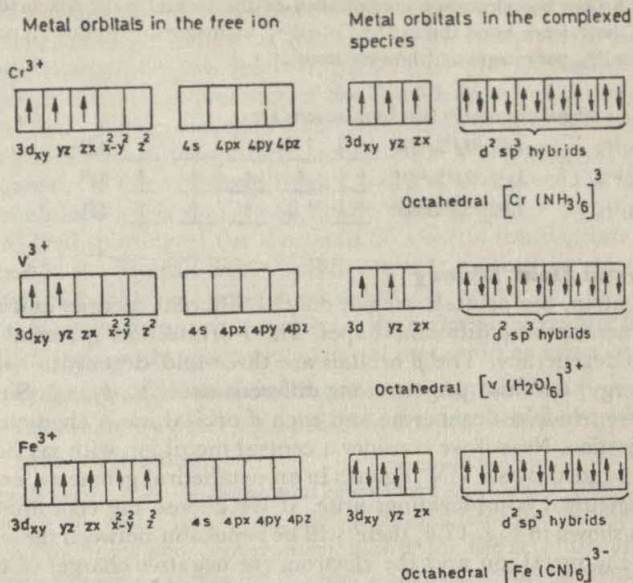
Fig. 17.3 Scheme for the bonding of octahedral complexes of transition metals using d^2sp^3 hybridisation of the metal orbitals

In order to explain the magnetic behaviour of certain complexes, the use of the outer $4d$ levels is made for constructing hybrid orbitals. In this case, octahedral geometry is achieved via $(4s)(4p)^3(4d)^2$ hybridisation, leaving $3d$ orbitals unhybridised. For example, it is seen that $[Mn(oxalate)_3]^{3-}$ has a magnetic moment of 4·81 magnetons. This has been explained by using the 'outer orbital' hybridisation, i.e. $(4s)(4p)^3(4d)^2$, which leaves the four $3d$ electrons of Mn (III) in four separate $3d$ orbitals, obeying Hund's rule. On the other hand, the complex $[Mn(CN)_6]^{3-}$ has a magnetic moment of 3·18 magnetons. This is rationalised by utilising the $3d$ orbitals in hybridisation as the 'inner orbital' hybrids $(3d)^2(4s)(4p)^3$. The four $3d$ electrons in Mn (III) will now be accommodated in the remaining three unhybridised $3d$ orbitals. This leaves two unpaired electrons and two paired electrons in the $3d$ levels, giving a total magnetic moment corresponding to two unpaired spins, i.e. 3·18 magnetons.

Tetrahedral complexes are formed by hybridising $4s$ and three $4p$ orbitals (sp^3). On doing so, the hybrid orbitals are pointed towards the corners of a tetrahedron. There are no inner or outer orbital complexes in this case.

Square-planar complexes are formed by metal ions like, Cu^{2+}, Ni^{2+}, Co^{3+}, Pt^{2+} and Pd^{2+}. In this type of geometry, the hybridisation involves one of the $3d$ orbitals, $4s$ orbital and two of the three $4p$ orbitals resulting in dsp^2 hybrid orbitals. These point toward the corners of a square.

The valence bond theory explains the geometries and the magnetic moments of complexes. However, there are many anomalous cases where the theory cannot provide an acceptable explanation. Besides, this approach cannot satisfactorily explain the electronic spectra of complexes; that is, it does not explain why the transition metal ions are coloured. All these properties along with most of the anomalies are better explained by what is termed as the *crystal field theory*.

Example 17.8 Give the electronic configuration of the central metal ion in the following according to the valence bond theory: (*i*) $Co(en)^{3+}_3$, diamagnetic; (*ii*) CoF^{3-}_6, paramagnetic; and (*iii*) $Co(en)^{2+}_3$, paramagnetic (three-electrons).

The electronic configurations of cobalt in these ions are:

(*i*) $Co(en)^{3+}_3$ $1s^2 2s^2 2p^6 3s^2 3p^6$ ↑↓ ↑↓ ↑↓ __ __ $3d^6$

(*ii*) $Co(F_6)^{3-}$ $1s^2 2s^2 2p^6 3s^2 3p^6$ ↑↓ ↑ ↑ ↑ ↑ $3d^6$

(*iii*) $Co(en)^{2+}_3$ $1s^2 2s^2 2p^6 3s^2 3p^6$ ↑↓ ↑↓ ↑ ↑ ↑ $3d^7$

17.3.3 Crystal Field Theory

In a given atom, the orbitals are not only of different energies ¡but also of different degeneracies and different shapes. The *s* orbital has spherical symmetry and has no degeneracy. The *p* orbitals are three-fold degenerate (three levels of same energy) and also project along different axes (p_x, p_y, p_z). Similarly the *d* orbitals are five-fold degenerate and each *d* orbital has a characteristic geometric projection. Now if we consider a central metal ion with say $3d^2$ configuration, surrounded by six CN^- ligands in an octahedral geometry, certain interesting geometrical considerations arise. If we choose the coordinates for the complex as shown in Fig. 17.4, there will be repulsion between the electrons in $3d$ level of the metal ion and the electrons (or negative charge) of the ligand.
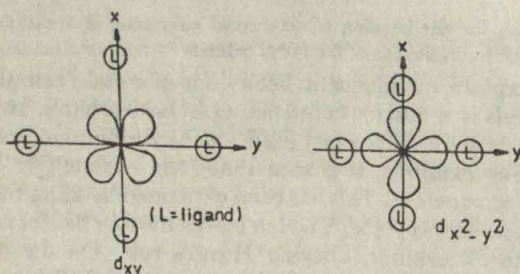
Fig. 17.4 Crystal field effects of ligands on the metal orbitals

We may also notice that such a repulsion is more when the $3d$ orbital is directed towards the ligand than when it is away from the ligand. Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals, which point towards the axes along the direction of the ligands will experience the ligand field repulsion and will be raised in energy (*destabilised*); and the d_{xy}, d_{yz} and d_{xz} orbitals will be *stabilised* in comparison. We may depict the situation as follows:
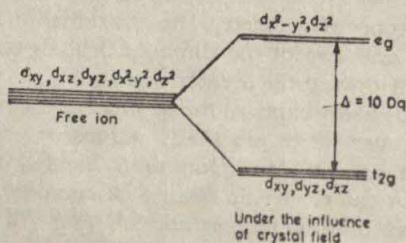
The five-fold degeneracy of the d levels has been removed due to ligand-electron–metal-electron repulsion in the octahedral complex to yield three levels of lower energy and two levels of higher energy. This splitting of the degenerate levels due to the presence of the ligands in a definite geometry is termed *crystal field splitting* and the extent of the split is usually denoted by Δ or $10\ Dq$ (where Dq is an energy term, constant for a given ligand-metal pair in a given geometry). The stabilised levels d_{xy}, d_{yz}, d_{xz} are given the notation t_{2g} while the destabilised levels $d_{x^2-y^2}$ and d_{z^2} are termed e_g.

The crystal field splitting of the d orbitals of a metal ion depends upon the field produced by the ligands. Some ligands are able to produce stronger fields in which case, the splitting (designated as $10\ Dq$ or Δ) will be large. In general, ligands can be arranged in a series in the order of increasing fields (and splitting) which they produce around a central metal ion as given below:

cyanide > ethylene-diamine > ammonia > pyridine >

thiocyanate > water > fluoride > hydroxide > chloride >

bromide > iodide

Such a series is termed as *spectrochemical series*. The splitting is also dependent on the nature of the metal ion. Thus, the splitting is least for the metal ions of the first transition series and progressively higher for the second and the third transition series elements ($10\ Dq$ for the first transition series elements $< 10\ Dq$ for the second series elements $< 10\ Dq$ for the third series elements). The third factor that affects the value of $10\ Dq$ or Δ is the charge or the oxidation state of the metal ion. For a particular metal ion, the higher the oxidation state, larger is the value of $10\ Dq$.

The foregoing considerations permit us to assign electrons in the d orbitals of metal ions in octahedral complexes. They would first be distributed in the t_{2g} (lower energy) levels, and after these are filled will occupy the e_g levels. The cases of $3d^1$, $3d^2$ and $3d^3$ electrons are clear. The $3d$ electrons can be distributed one each, as per Hund's rule, in each of the t_{2g} levels. When we come to the $3d^4$ case, the fourth electron can be placed either in the t_{2g} level (spin paired with one electron there), or can be placed in an e_g orbital. Two factors govern this choice: the crystal field splitting (Δ or $10\ Dq$), and the electron pairing energy P. If the value of P is less than $10\ Dq$, the fourth electron will remain in a t_{2g} orbital with its spin paired. This will result in a reduction of the magnetic moment of the complex, and the complex will be termed a *low-spin* complex. Alternatively, if $P > 10\ Dq$, the electron will find it easier to fill an e_g level and the total spin and magnetic moment of the complex will increase. Such a complex is referred to as a *high-spin* complex. Since the value of $10\ Dq$ for a given metal ion in a given geometry depends on the field of the ligand, it is seen that a ligand that produces a large splitting (e.g. CN^-) will produce a *low-spin* complex. Similarly, a metal ion coordinated by ligands that display a weak field (low $10\ Dq$, such as F^-) will be a high-spin complex. Therefore, complexes with *strong-field* ligands will be of the *low-spin* type and those with *weak-field* will be of the *high-spin* variety. Fe^{3+} ($3d^5$ configuration) forms octahedral complexes with F^- (weak field) and with CN^- (strong field ligand). In the former, the splitting $10\ Dq$ is smaller than the electron pairing energy and the five electrons will be populated in the complex as $(t_{2g})^3 (e_g)^2$, with all electrons unpaired, and the magnetic moment of FeF_6^{3-} is 5·9 magnetons. On the other hand, CN^- produces a splitting five times as large as F^-, In this case,

the five $3d$ electrons of Fe^{3+} will have the configuration $(t_{2g})^5 (e_g)^0$. The magnetic moment of $Fe(CN)^{3+}_6$ is 1·7 magnetons.

In tetrahedral complexes, the splitting of the metal d orbitals is opposite to that in the octahedral case. The $d_{x^2-y^2}$ and d_{z^2} levels are lowered while d_{xy}, d_{yz} and d_{zx} are destabilised. But otherwise the same factors govern the splitting energy and the magnetic properties of the tetrahedral complexes, as in octahedral ones. The splitting in tetrahedral geometry is smaller and thus only high-spin complexes are generally known for the first transition series of metals.

Example 17.9 For Mn^{3+}, the electron pairing energy, P is about 81 kcal mol^{-1}. 10 Dq values for the complexes $[Mn(H_2O)_6]^{3-}$ and $[Mn(CN)_6]^{3-}$ are 60 kcal mol^{-1} and 110 kcal mol^{-1} respectively. Do these complexes have high-spin or low-spin configurations?

Mn^{3+} is a d^4 system. After filling three electrons in t_{2g} orbitals, the fourth electron can go either in e_g or pair up with one of the electrons in t_{2g} depending upon the relative values of 10 Dq and P. If $P < 10 Dq$, the fourth electron will pair up, and in case $P > 10 Dq$, it will occupy e_g orbital Therefore,

    (*i*) in the complex $[Mn(H_2O)_6]^{3+}$, the configuration of Mn^{3+} is $t_{2g}^3 e_g^1$ ($P > 10 Dq$) and

    (*ii*) in the complex $[Mn(CN)_6]^{3-}$ the configuration of Mn^{3+} is $t_{2g}^4 e_g^0$ ($P < 10Dq$).

17.3.4 Colours of Transition Metal Complexes

A substance looks visibly coloured if it absorbs light in one region of the visible range of light and transmits the rest. Thus a compound that absorbs light in the yellow-red region (6000–7500 A) of the spectrum, transmits the rest and appears green in colour. One that does not absorb light in any part of the visible region appears colourless. During such an absorption process, electrons in the molecule get excited to higher energy states, and this phenomenon is referred to as electronic absorption spectroscopy (see Chapter 4).

Many of the transition metal complexes are coloured in the visible region. This colour is readily explained in terms of the crystal field theory. Consider for example the complex $[Ti (H_2O)_6]^{3+}$, which is violet in colour. This is an octahedral complex where the single electron (Ti^{3+} is a $3d^1$ system) in the metal d orbital is in the t_{2g} level in the ground state of the complex. The next higher state available for the electron is the empty e_g level, which lies at an energy of 4×10^{-12} ergs (or 20,000 cm^{-1} wave numbers) above the t_{2g} level. If light corresponding to this energy of 20,000 cm^{-1} (or 5000 A, greenish-yellow region) were impinged on the molecule, it would excite the electron from the t_{2g} to the e_g level ($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$); or if 'white' light were to be impinged on this complex, absorption of 5000 A radiation will occur, and the rest transmitted. Consequently, the complex appears violet in colour. The crystal field theory attributes the colour of this transition metal complex to $d \rightarrow d$ transition of the electrons.

It is noteworthy that since in the absence of the ligand, crystal field splitting of the $3d$ levels does not occur, the free metal ion itself should not be coloured. Removal of water by heating $Ti (H_2O)_6Cl_3$ indeed yields white $TiCl_3$. For the same reason, while anhydrous $CuSO_4$ is white, $CuSO_4·5H_2O$ is blue in colour. It may also be seen that the stronger the ligand field is, the larger the splitting and shorter will be the absorption wavelength. This is the basis behind the spectrochemical series of the ligands that we mentioned earlier. The chloride

complex of a given metal ion will be expected to absorb at a lower frequency (higher wavelength) than the cyanide complex, since the former ligand is one of weak-field and causes a smaller splitting (10 Dq) than the latter.

Example 17.10 $[TiX_6]^{3+}$ complex is violet. What change in colour would you expect if the ligand, X, in this complex were replaced by a ligand, Y that produces a stronger field?

It is a d^1 system where the transition is $t^1_{2g} \rightarrow e^1_g$ which corresponds to 10 Dq and the colour of the complex corresponds to light transmitted. Thus, by replacing the ligand X by Y, the value of 10 Dq will be increased, and it will absorb radiations of shorter wavelength. In other words, the complex will absorb in the ultraviolet region and hence appear colourless.

The crystal field theory is an oversimplification, since it treats the ligands as point charges or as dipoles. This allows for only electrostatic interactions between the metal and the ligand, but not any overlap of the metal orbitals with ligand orbitals. A more rigorous treatment should include bond formation (σ bonds or π bonds) between the metal ion and the donor. Such a treatment is termed *ligand field theory* and is in greater accord with experimental observations. Consider the octahedral complex $[Ti(H_2O)_6]^{3+}$. In the coordinate system previously chosen, the $d_{x^2-y^2}$ and $d_{z^2-r^2}$ orbitals of Ti^{3+} are directed towards the ligand molecules H_2O. In ligand field theory, one constructs molecular orbitals comprised of these d orbitals and the sp^3 orbitals of oxygen of the water to produce two bonding σ molecular orbitals and two antibonding σ^* molecular orbitals. The other three d orbitals, d_{xy}, d_{yz}, and dx_z, of the metal do not overlap with H_2O orbitals (directed away from the coordinate axes), and remain as non-bonding orbitals. Thus, the ligand field produces a splitting in the metal orbitals as three lower and two upper (σ^*) levels, much the same way as the crystal field theory does. The optical and magnetic properties are explained in a similar fashion, except that the transitions from t_{2g} to e_g levels now are interpreted to occur between nonbonding levels and antibonding orbitals. The splitting of the metal orbitals arises from the antibonding character of levels rather than simple charge repulsion. The treatment of tetrahedral and other complexes is done in a similar fashion.

17.3.5 Stabilities of Complexes

As mentioned earlier, the reaction between a metal ion and its ligands may be viewed as a Lewis acid-Lewis base reaction (Chapter 11). If the interaction between them is strong, the complex formed would be thermodynamically stable. Complexation depends on several factors such as the charge density of the ion, basicity of the ligand, and the electronic configuration of the metal ion and so on. The reaction between the metal and the ligand can be written as

$$M^{n+} + xL^{m-} \rightleftharpoons [ML_x]^{p+}$$
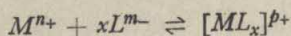
with an equilibrium constant K (see Chapters 10 and 11 for a discussion of equilibria). Since we are concerned more about the *instability* or *lability* of the complex, it is more convenient to define the reciprocal of the equilibrium constant, termed the *instability constant*:

$$K_{ins} = \frac{[M^{n+}]\ [L^{m-}]^x}{[ML_x]^{p+}}$$

The superscripts $n+, m-$ and $p+$ are written such that $(n+) + (m-) = (p+)$ for charge balance. The value of K_{ins} gives us an idea of the extent to which a

Table 17.6 Instability Constants of Some Metal Complexes

System	K_{ins} (25°C)
$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2\,NH_3$	$6\cdot3 \times 10^{-8}$
$[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4\,NH_3$	$2\cdot2 \times 10^{-13}$
$[Cu(CN)_4]^{2-} \rightleftharpoons Cu^{2+} + 4\,CN^-$	$5\cdot0 \times 10^{-28}$
$[Co(NH_3)_6]^{3+} \rightleftharpoons Co^{3+} + 6\,NH_3$	$2\cdot0 \times 10^{-34}$

given complex breaks down. Table 17.6 gives the instability constants of some complexes.

Complexes with a low values of K_{ins} will exist predominantly in the coordinated form in solution, while those with high values of K_{ins} will have a significant fraction of free metal ions, i.e. the larger the instability constant, the greater the tendency for the complex to dissociate. We notice from the table that the silver-ammonia complex is less stable than the cobalt complex. This is due to the fact that silver has its d levels filled completely, while cobalt has unfilled $3d$ levels. In the first transition series, complexes of Mn^{2+} are, for the same reason, expected to have smaller values of K_{ins} than those of Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} in that order. It is also seen from the table that the cyanide complex of copper is more stable (smaller K_{ins}) than the ammonia complex. This is due to the stronger Lewis base strength of CN^- compared to NH_3. A consequence of this is the lability of complexes, wherein ligands can be substituted by an exchange process. For example, in the reaction occurring in aqueous

$$[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4\,NH_3$$
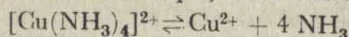
solution, the copper ions are not free but exist as hydrated species $[Cu(H_2O)_4]^{2+}$. The actual reaction is thus a substitution of the liganded water molecules by ammonia.

$$[Cu(H_2O)_4]^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$
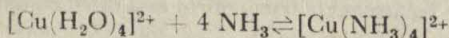
The equilibrium constant for this process is what is reflected as the (reverse of the) instability constant of the Cu(II)-ammonia complex. This is reasonable since in the spectrochemical series, water appears as a weaker-field ligand than ammonia.

While some complexes may be quite stable, the metal-ligand bond may be of such strength as to make it labile. An example is $[Ni(CN)_4]^{2-}$ which is stable ($K_{ins} = 10^{-22}$) and yet, addition of radioactive $^{14}CN^-$ ions to an aqueous solution of the complex gives a completely radioactive complex of the same formula $[Ni(^{14}CN)_4]^{2-}$

SUGGESTED READING

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F. A. COTTON and G. WILKINSON, *Advanced Inorganic Chemistry*, Second edition, John Wiley, New York (1966).

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E. M. LARSEN, *Transitional Elements*, W. A. Benjamin, Inc., New York (1965).

PROBLEMS

17.1 Classify the following ions or elements as d-block transition metal ions or elements, lanthanide ions or elements, actinide ions or elements and non-transitional metal ions:

Ca^{2+}, Sc^{3+}, Sc, Cu^+, Cu^{2+}, Ni^{4+}, Pt^{4+}, Pd^{2+}, Au^{3+}, Zn^{2+},

Zu, Cu, Ti^{4+}, Ru, Ru^{3+}, Os^{4+}, Gd, Gd^{3+}, Cr, Cf, Cf^{4+},

Hg^+, Tl^+, Ce^{4+}, Nb, Ta^{5+}, MO^{6+}, U, Hn, Fm, and Mv.

17.2 How are the d orbitals involved in the metallic bonding and why do they affect the metallic bond strength?

17.3 Why do $5s$- and $6s$-electrons have similar ionisation energies, while $4s$-electrons have higher ionisation energies?

17.4 Why is Cu^+ unstable in aqueous solution?

17.5 Will Ti^{3+} disproportionate to Ti^{2+} and TiO^{2+} in acid solution?

17.6 Explain the following observations: (i) In photography, the fixing bath ($Na_2S_2O_3$) dissolves $AgBr$ from the film. (ii) Gold is oxidised by O_2 when NaCN is present. (iii) Platinum metals do not react with nitric acid, but react with aqua-regia ($HNO_3 + HCl$).

17.7 The standard potential for: $VO^{2+} + 2 H^+ + e \rightleftharpoons V^{3+} + H_2O$, $E°red = -0.36$ V. Are solutions of V^{3+} subject to air oxidation?

17.8 The *volcano experiment* involves heating a mound of the orange solid $(NH_4)_2Cr_2O_7$. Among the products are a large volume of the green solid, Cr_2O_3, and N_2 gas. Write the equation for the reaction.

17.9 Explain why in the whole sequence of lanthanide elements trivalency is predominant.

17.10 Suppose we discover elements in which the $5g$ orbital is being filled. What should be the general characteristics of these elements?

17.11 What are the shapes of the following molecules? $SnCl_4$, $HgCl_2$, $CuCl_2$, $NbCl_5$, $ZrCl_4$, $FeCl_3$, $HgCl$, OsO_4, CrO^{2-}_4? Indicate the bonding wherever possible.

17.12 (i) Draw the unit cell of NiO (NaCl structure) and indicate how antiferromagnetism may arise in this compound.

(ii) Draw a cell of Fe_3O_4 and show how ferrimagnetism can be pictured in this compound.

17.13 Give example of bi-, tri-, and tetra-dentate ligands.

17.14 How do the size of the metal ion, and the nature and the structure of the ligand molecule affect the coordination number and the structure of a complex?

17.15 List the possible potential isomers of the compound $Co(NH_3)_6 \cdot Cr(CN)_6$.

17.16 Which of the five d orbitals ought to be used for dsp_2 hybridisation?

17.17 (i) Write on a piece of paper with a colourless ink made of a solution of $CoCl_2 \cdot 6H_2O$. Let it dry for a short time and then heat the paper over a mild flame. The invisible writing becomes blue-coloured. Why?

(ii) Why does a light blue coloured solution of copper sulphate become green upon the addition of concentrated HCl?

(iii) Why is $CaCl_2$ colourless both in crystal and in aqueous solution?

17.18 How will you qualitatively explain the splitting of the d orbitals in square-planar geometry?

17.19 Suggest a low- and high-spin state electron distribution for a d^4 ion in a tetrahedral crystalline field.

17.20 (i) Draw the geometrical isomers of $Cr(H_2O)_3F_3$ and $[PdBrCl_2I]^{2-}$.

(ii) Ethylenediamine is a bidentate ligand abbreviated as 'en'. Which of the following can exist as optical isomer:

$[Co(NH_3)_4en]^{3+}$, *cis*- $[Co(NH_3)_2en_2]^{3+}$, and *trans*- $[Co(NH_3)_2en]^{3+}$?

17.21 What are the orbitals involved in the formation of $[Ni(CN)_4]^{2-}$, a square-planar complex? Calculate the magnetic moment of the complex.

18

Chemistry of
the Living Cell

Despite these uncertainties we feel that our proposed structure for deoxyribonucleic acid may help to solve one of the fundamental biological problems—the molecular basis of the template needed for genetic replication. The hypothesis we are suggesting is that the template is the pattern of bases formed by one chain of the deoxyribonucleic acid and that the gene contains a complementary pair of such templates.

J. D. WATSON AND F. H. C. CRICK (1953)

In this chapter, we shall deal with the chemical processes important to life. The *cell* is the ultimate unit of any form of life. Cells associate to form *tissues*; tissue organisation leads to limbs and organs; and an *organism* develops as an assembly of organs. Thus, in order to understand the functioning of organisms from the chemical point of view, we have to study and understand the chemical processes occurring in biological cells. Such a study of the chemistry of the living cell is usually referred to as *biochemistry*. Even though at the organisational and functional levels a cell is a rather complex entity, the same principles of chemical bonding, thermodynamics, reaction mechanisms, and rate processes that we have encountered before operate at the cellular level as well. A biological cell, in fact, may be viewed as a miniature chemical factory. Energy is absorbed by the components of the cell, stored, converted and transferred. Chemical synthesis and degradation occur in various parts of the cell. Depending on what function a cell performs, the chemical and physical processes in it will vary. Thus, cells of different parts of the body will display different characteristics. And yet, understanding the physical and chemical processes in the cell will aid us in understanding biological processes at the level of the organism.

Not only cells from different species differ in characteristics and function, but the cells from different organs also differ from each other. Blood cells are spherical in shape while nerve cells are very long and cable-like. There is no 'typical' cell that can be described. However, despite this diversity, a variety of cells share many common structural features. We shall proceed to describe the cell in rather general terms.
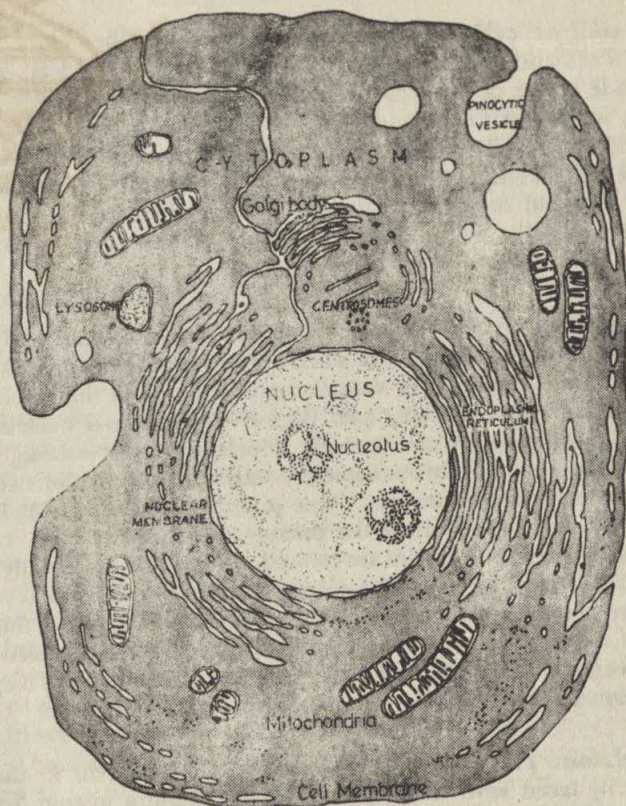
Fig. 18.1 Schematic illustration of a cell

18.1 THE CELL AND ITS COMPONENTS

Fig. 18.1 illustrates a rather generalised picture of a cell, its organelles, and its membrane structures. Such a composite picture of the cell has arisen by first breaking the cells open by gentle mechanical means (like a kitchen blender) and separating the various components by means of fractional *centrifugation.** The cell *nuclei* sediment first (being heaviest) when the centrifugal force is about a thousand times that of gravity (1000 g), followed by the *mitochondria* (10^4 g), the *lysosomes* (3×10^4 g), and the *ribosomes* (10^5 g), while the supernatant solution is a 'soup' that contains many molecules, big and small. Electron micrographs of tissues, cells and cell components have given excellent details of the organisation of the cell (i.e. the micro- and the ultra-structures). A brief summary of the various parts and their functions is given below.

*The cells are suspended in salt solution in a suitable container attached to a high speed rotor motor. The motor is allowed to rotate at speeds as high as 70,000 revolutions per minute. Under such conditions, the force experienced by the particles in the cell are as high as 500,000 times that of gravity (5×10^5 g). At low rotor speeds, the heaviest particles sediment to the bottom of the container and as the speed is gradually increased, lighter particles tend to sediment.

The cell wall or cell membrane: This forms the boundary between the interior of a cell and its surroundings. In plant cells, the cell wall is inert and is usually made of the polysaccharide *cellulose*. Animal cells possess a cell membrane that is thought to be made up of a bimolecular layer of proteins in the exterior and certain oil-soluble organic compounds (broadly classified as *lipids*) inside. The cell membrane acts as a selectively permeable unit that allows the passage of ions and small molecules across itself. The thickness of such a cell membrane is usually about 100 A. The cell membrane is quite an elastic entity as seen especially during cell division.

Cell nucleus: In the centre of a cell, one sees a roughly spherical body about several hundred angstroms in size surrounded by a thin membrane that has holes (pores) in it allowing for communication between this nucleus and the rest of the cell termed the *cytoplasm*. Within this spheroid nucleus, one finds rod-shaped substances called *chromatin* which form *chromosomes* during cell division. Analysis of the chromosomes reveals the presence of two polymeric chemicals: *nucleic acids* and *proteins*. While plant cell nuclei are rich in *ribonucleic acid* (RNA), animal cells show the presence of *deoxyribonucleic acid* (DNA). Proteins found within the nuclei are termed *histones* and are usually rich in the amino acids *lysine* and *arginine*. The genetic information of a cell is stored in the nuclear chromosome, particularly, DNA. It is now established that the basic genetic unit, called the *gene*, is in fact a part of the DNA molecule. As we will see later, duplication and synthesis of DNA and also the synthesis of a special form of RNA (known as *messenger RNA*) occur in the cell nucleus.

Mitochondrion: These are shoe-shaped bodies that occur in the cell cytoplasm, heavily laced with membranes. Usually about a micron long and half as thick, there are hundreds of mitochondria in a cell. The main constituents are membrane lipids, hundreds of enzymes and a small amount of DNA. Oxidation of sugars into smaller chemicals, CO_2 and H_2O (which is the main metabolic source of energy) and production of the energy rich molecules called *ATP* occur in mitochondria. The mitochondrion is hence viewed as the 'machine' or the 'battery' of the cell. Correspondingly, in plant cells, we find organelles called *chloroplasts* which are lamellar structures where photosynthetic reactions take place.

Ribosomes: Usually in their biologically active states, these spherical particles (150 A diameter) associate to form structures called *polysomes*. Ribosomes are generally found attached to the channel-like *endoplasmic reticulum*. The chief constituents of ribosomes are a special form of RNA known as *ribosomal RNA*, proteins, and enzymes (especially of the type that catalyse the synthesis of proteins). Ribosomes are the sites where synthesis of proteins and enzymes occurs.

Endoplasmic reticulum: This is a broad canal that extends as a long tube from the nuclear membrane pores into the main body of the cytoplasm. Transport of molecules and small chemicals is effected through the reticulum. Along the channel are found bags called *cisternae* that separate the cytoplasmic substances into phases. Along the membrane walls of the reticulum sit the ribosomes mentioned earlier.

Lysosomes: These are heterogeneous set of granular particles containing substances which digest large molecules into smaller units. Mechanical digestion also occurs when large molecules enter the lysosomes.

For our purpose, the important chemical and physical processes in the cell occur in the *cell nucleus, ribosomes, mitochondria and chloroplasts*. These processes are, respectively, duplication and production of DNA and messenger RNA, synthesis of proteins, food *metabolism* and *oxidative phosphorylation*, and *photosynthesis*.

18.2 CHEMICALS INSIDE THE CELL : LARGE MOLECULES

Depending on the kind, function and species, the chemical constituents of a cell vary. As an illustrative example, we shall examine the general features of the cell of the bacterium *Eschericia coli*. At the molecular level, E. coli is perhaps the best understood cell and a study of its cellular processes would provide a composite picture of all aspects of biology that we shall be concerned with. In a proper growth medium (i.e. with proper food), the E. coli cell doubles itself in 20 minutes (generation time), while on a ' bad diet ', the generation time is about an hour and a half. This means that a variety of degradative and synthetic pathways exist in the cell, all leading to proper growth and duplication. The cell derives its energy and capacity to function by a series of properly organised chemical reactions where food molecules are degraded into their most basic constituents and the accompanying energy is stored not as heat but as chemical free energy in the form of certain ' high energy ' compounds.

Regenerations of cell materials (i.e. *biosynthesis* of small and large molecules) that are used both as functional and as architectural ' raw material ' are chemical processes. In its chemistry, the cell uses a class of proteins known as *enzymes* which catalyse bioreactions. For the synthesis of the enzymes themselves, and for the duplication of the cell, another special class of polymers called nucleic acids are used. Reserve energy is also stored in the form of polysaccharides such as glycogen; some polysaccharides such as cellulose, are used as construction materials for the cell wall and other components. The cell stores all the chemicals it requires for these functions within itself. Verily, the cell is a storehouse of several thousand molecules, small and big, which are constantly produced and used up. Table 18.1 gives the approximate chemical composition of an E. Coli cell, in its rapidly dividing stage.

18.2.1 Polysaccharides

Polysaccharides are high molecular mass polymers where the repeating monomeric units are sugars, usually 6-carbon hexoses such as *glucose, galactose*, and *fructose*. Polymerisation is achieved through ether linkages formed between the hydroxy groups of neighbouring hexose monomers. For example, in the *polyglycan* given below, the ' backbone ' is a 1 : 4 linkage between neighbouring monomers.
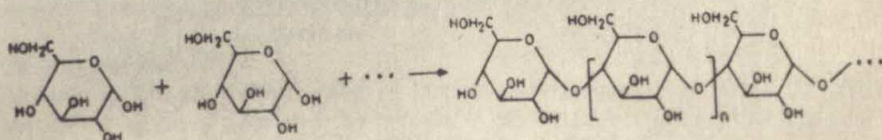
Table 18.1 Chemical Composition of a Rapidly Dividing E. coli Cell

Component	% of cell mass	Average molecular mass	Approximate number per cell	Number of different kinds
Water	70	18	4×10^{10}	1
Inorganic ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Cl^-, PO^{3-}_4, SO^{2-}_4)	1	40	2.5×10^8	20
Carbohydrates + Precursors	3	150	2×10^8	200
Amino acids + Precursors	0.4	120	3×10^7	100
Nucleotides + Precursors	0.4	300	1.2×10^7	200
Lipids + Precursors	2	750	2.5×10^7	50
Other small molecules	0.2	150	1.5×10^7	200
Proteins	15	40,000	10^6	2000–3000
Nucleic acids				
DNA	1	2.5×10^9	4	1
r-RNA	6	$5 \times 10^5 – 1 \times 10^6$	6×10^4	2
s-RNA		25000	4×10^5	40
m-RNA		10^6	10^3	10^3

Notice that each monomer is really pentafunctional (i.e. has five groups available for polymerisation). This polyfunctionality would lead, in general, to severe branching in the end product. In nature, one finds linear polysaccharide chains such as *cellulose* and *amylose* where there is very little chain branching and branched polyglycans such as *amylopectin* where both 1 : 4 and 1 : 6 sugar linkages occur; in *chondroitin sulphates*, one notices 1 : 3 linkages besides 1 : 4 linkages.

linear, 1:4 linkages
(amylose)

branched, 1:4 and 1:6 linkages
(amylopectin)

glucose and its
derivatives

1:4 , 1:3 linkages
(chondroitin sulphate)
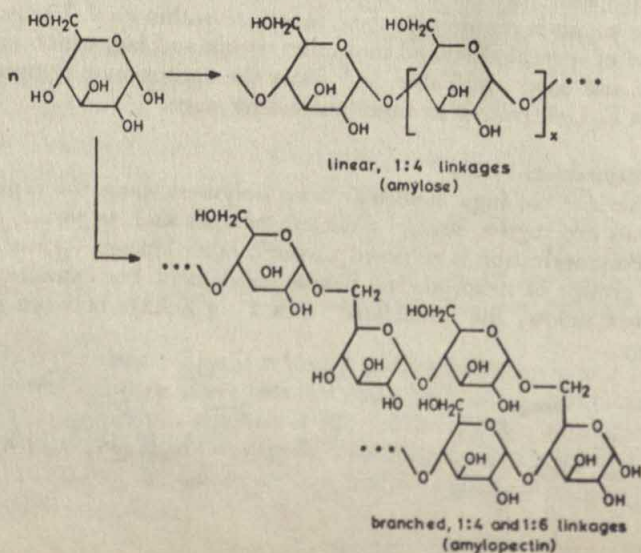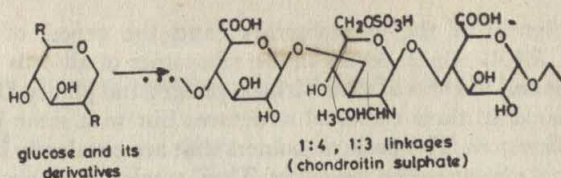
Polysaccharides encountered in animal and plant cells usually function as food, ground substance, cell wall material, material in tissues, cartilage, etc., and also as blood group substances. Table 18.2 lists several important polysaccharides encountered in living cells, along with their functions.

Table 18.2 Polysaccharides and their Functions in Cells

Name of the polysaccharide	Chemical constituents and features	Occurrence	Functions
Cellulose	1:4 linked glucan	Plants, microbes	Cell wall material, food
Starch	1:4, 1:6 link glucan	Plants.	Food
Glycogen	1:4, 1:6 link glucan	Animals	Food
Pectin	Galactose polymer	Cell walls and plant cytoplasm	Gelating agent
Hyaluronic acid	1:4, 1:3 links N-acetyl glucos-amine	Ground substance in animals cells	Glue or cement
Chondroitin sulphates	Glucuronic acid 4-6 sulphates esters of N-acetyl glucosamine	Cartilages and tendons	Polyelectrolyte
Heparin	Glucosamine sul-phate, glucuronic acid	Liver tissue	Anticoagulant of blood

One of the staple foods that we eat is the polysaccharide *starch* (*amylose* and *amylopectin*). It is first degraded by the salivary and gastric fluids to the hexose sugar glucose (see section 18.4.1). Oxidation of glucose to carbon dioxide and water by a series of involved steps yields energy for biological processes in the cell.

The important class of biological polymers, the nucleic acids, also have certain monomeric sugars as basic constituents. Ribonucleic acid consists of a ' back-bone ' made up of the pentose sugar units, *d-ribose*, linked to one another via *phosphodiester bonds*, while deoxyribonucleic acid uses *2-deoxy-d-ribose* units joined together by phosphodiester links (see section 18.2.2). It is interesting that most naturally occurring polysaccharides are comprised of monomeric sugars of the optically active *d*-configuration only.

18.2.2 Nucleic Acids

Nucleic acids are polymers ranging in molecular masses from 10^4 to 10^9, that are found in the nucleus and the cytoplasm of cells. Two types of nucleic acids are known: *Deoxyribonucleic acid* (*DNA*) that is found in the cell nucleus as the

constituent polymer of the chromosomes (and the genes) of animals, and *ribonucleic acid* (*RNA*) which occurs in the ribosomes of all cells and in several instances, in the cell nucleus of some viruses, phages and plants. DNA and RNA are closely related in their chemical structures but with some important distinguishing differences. The basic monomers that are covalently linked together to give nucleic acids are called *nucleotides*. Thus, nucleic acids are *polynucleotides*; the monomeric unit of DNA is referred to as a *deoxyribonucleotide* while that of RNA is a *ribonucleotide*.

Deoxyribonucleotide   Ribonucleotide
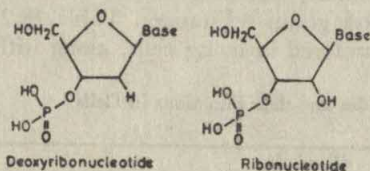
A ribonucleotide has the *d*-ribose sugar moiety, with a phosphate group at the 3′ position, a —CH_2 group at the 5′ end and a heterocyclic base attached in the 1′ position. A deoxyribonucleotide differs from its ribo-analogue in the fact that here the 2′ position in the sugar part carries simply a hydrogen in place of a —OH of the latter, and also in the nature of the heterocyclic bases at the 1′ end.

The heterocylic bases at the 1′ end belong to the *purine* and *pyrimidine* classes. The purine bases occurring in nucleotides are *adenine* (*A*) and *guanine* (*G*). The pyrimidine bases are *cytosine* (*C*), *uracil* (*U*), and *thymine* (*T*).

(A)   (G)   (C)   (U)   (T)
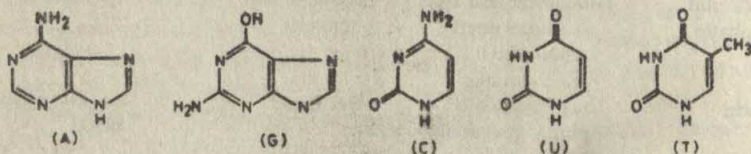
The bases *A*, *G*, *C* and *T* occur in deoxyribonucleotides and DNA while ribonucleotides and RNA consist of the bases *A*, *G*, *C* and *U*. Thus, the basic chemical differences between DNA and RNA are: (*i*) the sugar moiety in RNA is *d*-ribose, while the sugar in DNA is 2-deoxy *d*-ribose and (*ii*) while the bases *A*, *G*, and *C* are found both in DNA and RNA, the base *T* occurs only in DNA and the base *U* only in RNA. Polymerisation of monomeric nucleotides to form DNA and RNA occurs via phosphodiester bonds between the 3′ position of one monomer and the 5′ position of another (Fig. 18.2).

Chain conformations of nucleic acids: Nucleic acids are high polymers made up of sequential arrangements of four types of nucleotides. Since these nucleotide monomers differ from one another in their constituent bases, there is a great variety possible in the length and in the sequence of bases along the chain. Each nucleic acid differs from another in molecular mass and in the base sequence. Since the chain length is variable at will, there are indeed innumerable DNA (and similarly RNA) molecules possible. The chain conformations of the various DNA molecules seen in nature, however, are similar. Such an unity is not seen in the RNA molecules.
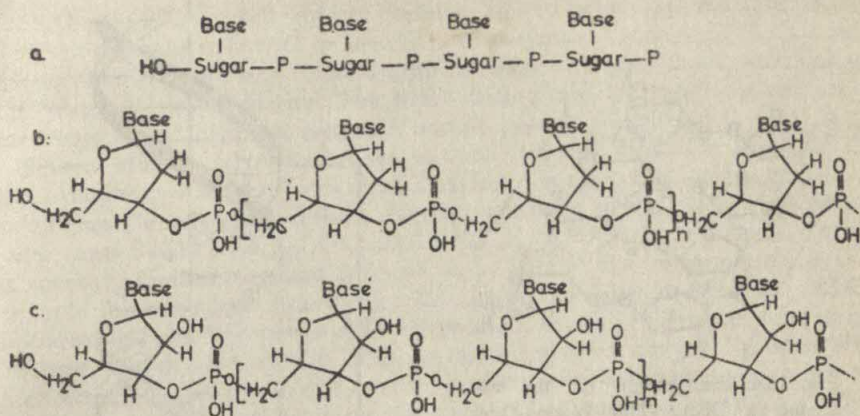
Fig. 18.2 Primary structures of (*a*) nucleic acids; (*b*) DNA; and (*c*) RNA

DNA: Chargaff made the remarkable observation that in DNA molecules from various sources, the base compositions show a regularity—the amount of A is always equal to that of T, G content is the same as that of C; further, the $(A+G)/(C+T)$ ratio is close to unity. That is, $A=T$, $G=C$, and $A+G=C+T$. It was also found that of the DNA bases, A forms specific hydrogen bonds with T, and G specifically hydrogen bonds with C. This is an important factor in the chain structure of DNA—and is usually referred to as *complementary base pairing* (Fig. 18.3). The bases A and T are referred to as complementary bases, as are G and C.
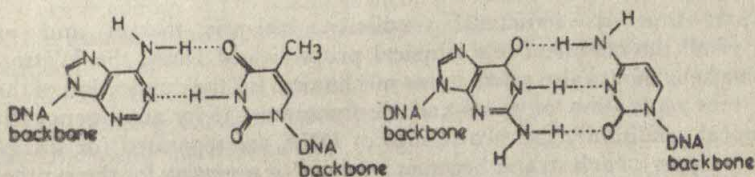
Fig. 18.3 Complementementary base pairing in DNA. A forms two hydrogen bonds with T and G forms three hydrogen bonds with C.

Utilising these facts as well as the x-ray diffraction data, Watson and Crick suggested a double stranded structure for the DNA molecule shown in Fig. 18·4. The Watson-Crick structure for DNA consists of two polynucleotide chains oriented in opposite directions (antiparallel), strung together into a *double-helical structure* somewhat like a twisted ladder. The width of the double helix is 20 A, and each turn of the helix (pitch) is 34 A (or the equivalent of 10 nucleotides). Each strand backbone is made up of the sugar (S) deoxyriboses linked by the 3'–5' phosphodiester bonds (P). Jutting out 90° from the sugar plane and pointing to the inside of the helix are the bases A,G,C and T. A from one strand is base-paired via hydrogen bonding to the T from the other strand (note the base pair complements $A=T$ and $G=C$). These hydrogen bonds offer a source of stability to and maintain the double helix (like the rungs of a ladder or steps of a spiral staircase). An additional source of stability for the double helix is the dipolar forces between bases along the helix axis. The base
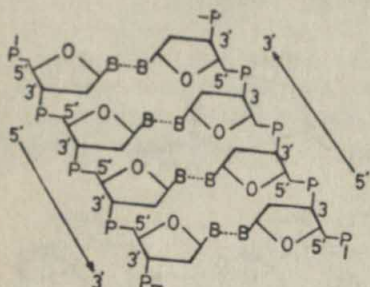
Fig. 18.4 Arrangement of the two chains in DNA. The Watson-Crick double helical structure of DNA molecules is shown on the right. S stands for the sugar deoxyribose, P for the phosphodiester moiety, and A, G, C, T the bases.
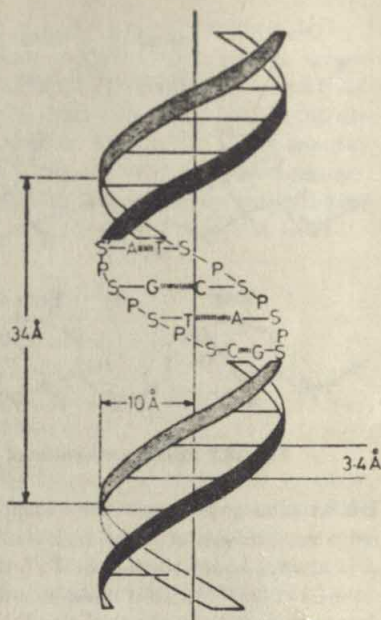
pairing relation thus imposes the idea of complementarity in the chains as well, i.e. one strand is complementary to the other in the DNA helix. If the base sequence of one strand is known, that of the other is automatically fixed because of this complementarity. If we view one strand as the ' lock ', the other strand is the ' key '.

Apart from its structural simplicity, intrinsic marvel and explanation of all the chemical and physical properties of DNA, the Watson-Crick double helix model also offers a neat mechanism for the duplication of the DNA and thus replication of genes and chromosomes. If by any agency (heat or chemical condition), the two strands of DNA are separated (or unzipped as from a zipper), each strand becomes a mould or a *template* for the synthesis of a new DNA strand from monomeric deoxyribonucleotides. If a separate strand has the base sequence $AGCTTAG$....... from the free 5' end on, the newly synthesised DNA chain will be $TCGAATC$.... from its free 3' end on. This is because of the $A = T$ and $G = C$ relationship. Thus, each strand produces its complement. We shall discuss this aspect in some detail later.

The Watson-Crick model thus suggests a long, thin rod or thread shape to DNA. DNA molecules isolated from natural sources are very long chains. For example, DNA from the thymus glands of calves have molecular masses as high as 10^7–10^8, and from E. coli, 10^9. In some bacteria and viruses, the DNA molecule is a complete circle (i.e. the double strand helix is a ring). Action of heat, extremes of pH, salt concentration changes and addition of certain *denaturants* break the inter-strand hydrogen bonds and cause *denaturation* of DNA yielding two separate strands, which by themselves are devoid of any structural regularity. This process of denaturation is referred to as the helix-coil transition or *melting*.

RNA: Studies on RNA reveal that some base pairing exists between A and U

(note that in RNA, uracil replaces thymine, T) and between G and C. But RNA does not show the A/U, G/C, or $A+G/U+C$ constancy as seen in DNA. It is also known that in most cases, RNA is simply a single stranded chain with none of the Watson-Crick regularity. The RNA single chain is thought to exist in a randomly folded form with some AU and GC pairing in regions.

Several kinds of RNA are known to occur in living cells. The *soluble RNA*, also called *transfer RNA* (*t*-RNA or *s*-RNA) found in the cytoplasm has relatively small chain length with less than 100 ribonucleotides in the chain. High molecular mass RNA called the ribosomal RNA or *r*-RNA, with a molecular mass of several hundred thousand is found to be part of the ribosomes along the endoplasmic reticulum. And a third kind known as *messenger RNA*, or *m*-RNA is known to be formed in the cell nucleus and is usually 1500 nucleotides long. In these cases of RNA, as with DNA, an innumerable variety of RNA molecules are formed, differing from one another in chain length and in the sequence of the bases A, G, C, and U along the chain. 'Denaturation' of RNA is also observed, but is not as dramatic or cooperative a phenomenon as in DNA. The importance of DNA and RNA in the genetics of the living cell will be discussed later.

It is worth pointing out here that most nucleic acids seen in the cell do not appear in the free chemical form, but are associated with a certain class of proteins called *histones*. Together, this nucleic acid–protein complex is referred to as *nucleoprotein*. In the chromosomes of cells, one finds the DNA associated with histones as complexes. The removal of the histone protein is easily achieved by the addition of salts or changes in pH.

Viruses which attack plant and animal cells are good example of nucleic acids associated with proteins. Most plant viruses have RNA and protein, and animal viruses are made up of DNA and protein. In these cases, as for example in a virus that attacks bacteria, called *bacteriophage*, the DNA is encapsulated inside a protein coat. Usually the phage is represented with a hexagonal 'head' inside which the DNA resides and a tail. The outer 'skin' of the head and the tail is protein. During bacterial infection, the virus opens up from its tail and injects DNA into the host cell.

18.2.3 Proteins
Besides polysaccharides and nucleic acids, the third and the most versatile class of polymers occurring in living cells are proteins. Proteins function in various ways in the cell as structural material like *collagen* and *keratin*, as molecular carriers like *hemoglobin*, *myoglobin* or polypeptides and as catalysts (enzymes) for the reactions occurring in the cell. Like the other two macromolecules, proteins are also made up of optically active constituents and are therefore optically active.

Proteins are macromolecules ranging in molecular mass from 10^3 to 10^7. The monomeric units that link together to form proteins are called *amino acids* and have the general formula, H_2N—$CH(R)$—$COOH$, where the side chain group R varies from one amino acid to another. There are about twenty amino acids that are known to constitute proteins. Amino acids occurring in proteins are generally of the optically active *l*-configuration. The simplest amino acid, glycine, where R is hydrogen (i.e. H_2N—CH_2—$COOH$) is not asymmetric or optically active. Occasionally, some amino acids of the *d*-configurations are found in proteins and more often in smaller molecular

mass proteins called *polypeptides*. Out of the twenty amino acids known to occur in nature, about eight have polar side chains (i.e. the R groups are ionisable or have polar character). The rest have nonpolar or hydrocarbon side chains, and since these hydrocarbon side chains possess no great attraction for the water dipole, are referred to as hydrophobic groups. The names, abbreviations and structure of amino acids are given in the Table 18.3.

Table 18.3 Common Amino Acids

GENERAL STRUCTURE OF AMINO ACIDS: $H_2N{-}CH{-}COOH$ with R on the CH

Amino acid	Abbreviation	$R =$
Glycine	gly	$-H$
Alanine	ala	$-CH_3$
Valine	val	$-CH{<}^{CH_3}_{CH_3}$
Leucine	leu	$-CH_2{-}CH{<}^{CH_3}_{CH_3}$
Isoleucine	ileu	$-CH{-}CH_2{-}CH_3$ with CH_3
Serine	ser	$-CH_2OH$
Threonine	thr	$-CH{<}^{OH}_{CH_3}$
Cysteine	cys	$-CH_2{-}SH$
Cystine		$-CH_2{-}S{-}S{-}CH_2{-}$
Methionine	met	$-CH_2{-}CH_2{-}S{-}CH_3$
Aspartic acid	asp	$-CH_2{-}COOH$
Asparagine	asn	$-CH_2{-}CONH_2$
Glutamic acid	glu	$-CH_2{-}CH_2{-}COOH$
Glutamine	gln	$-CH_2{-}CH_2{-}CONH_2$
Lysine	lys	$-(CH_2)_4{-}NH_2$
Arginine	arg	$-(CH_2)_3{-}NH{-}C{<}^{NH}_{NH_2}$
Histidine	his	
Phenylalanine	phe	
Tyrosine	tyr	
Tryptophan	try	

IMIONO ACIDS

Imino acid	Abbreviation	Structure
Proline	pro	
Hydroxyproline	hypro	

As with sugars and nucleotides, amino acids are also polyfunctional. That is, they have at least two functional groups, —NH$_2$ and —COOH. The amino acids in a protein molecule are linked together by *amide bonds* (peptide bonds), as shown below:

$$\underset{R_1}{H_2N-\overset{R_1}{CH}-COOH} + \underset{R_2}{H_2N-\overset{R_2}{CH}-COOH} \longrightarrow H + HN-\overset{R_1}{CH}-CO + HN-\overset{R_2}{CH}-CO + OH$$
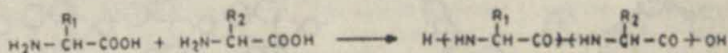
In a protein chain, therefore, we have,

$$H_2N-\overset{R_1}{CH}-CO-NH-\overset{R_2}{CH}-CO-NH-\overset{R_3}{CH}-CO-\cdots$$
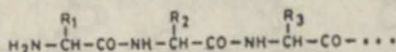
The basic monomeric unit of a protein is, therefore, represented by —(NH—CH—CO—). The amino group, NH$_2$, of one amino acid can
$$\underset{R}{|}$$
combine with the —COOH group of another forming a peptide. This process can keep on going *ad infinitum*, yielding a long polypeptide chain that is called a protein. One end of the protein will have a free —NH$_2$ group while the other end has a free —COOH group.

Proteins differ from one another in the length of the polypeptide chain (and hence the molecular mass) and the arrangement or sequence of the amino acids along the chain. Many proteins contain more than one polypeptide chain (i.e. multi-unit systems where each sub-unit is a polypeptide chain). For example, the oxygen-carrier protein, *hemoglobin*, consists of four polypeptide chains, labelled α_1, α_2, β_1, and β_2. The sub-unit polypeptide chains are held together by weak non-covalent forces. Dissociation of such a multimeric protein into its sub-units is achieved by mild treatment. Very often, covalent linkages of the —S—S disulphide type occur between the cysteine —SH side-chains of one chain with those of another. Such interchain disulphide bonds are seen in proteins such as insulin. Disulphide bridges within the same chain may also occur as shown below and these lead to a puckering or folding of the conformation of the molecule.
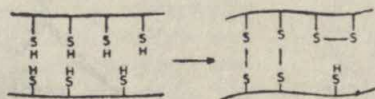
Conformations of proteins: The basic chemical structure, i.e. the sequence of the amino acids along the chain of the polypeptide, is referred to as the primary structure and is typically written as

$$H_2N-gly-cys-val-tyr-lys-asp-lys-\ldots$$
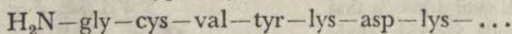
The primary structure defines the chemicals tructure of a protein, and also indirectly dictates the shape or the manner of folding of the polypeptide chain. As in the case of the nucleic acids, protein chains are also folded into definite conformations. Such folding of the polypeptide arises from, (*i*) hydrogen bonding between the peptide links in the same chain or sometimes between two chains, (*ii*) electrostatic interactions between charged side chain groups of the constituent amino acids in chains, and (*iii*) by interactions between nonpolar side chains of various amino acids in the same chain or between chains.

(a)

(b)

(c)

Fig. 18.5 (a) The α-helical conformation that occurs in proteins. R stands for side chain groups. (b) The β-pleated sheet conformation adopted by proteins from *Bombyx Mori*. (c) The solid state conformation of the enzyme Lysozyme. The shaded region depicts the area where the substrate sits when catalysis occurs.
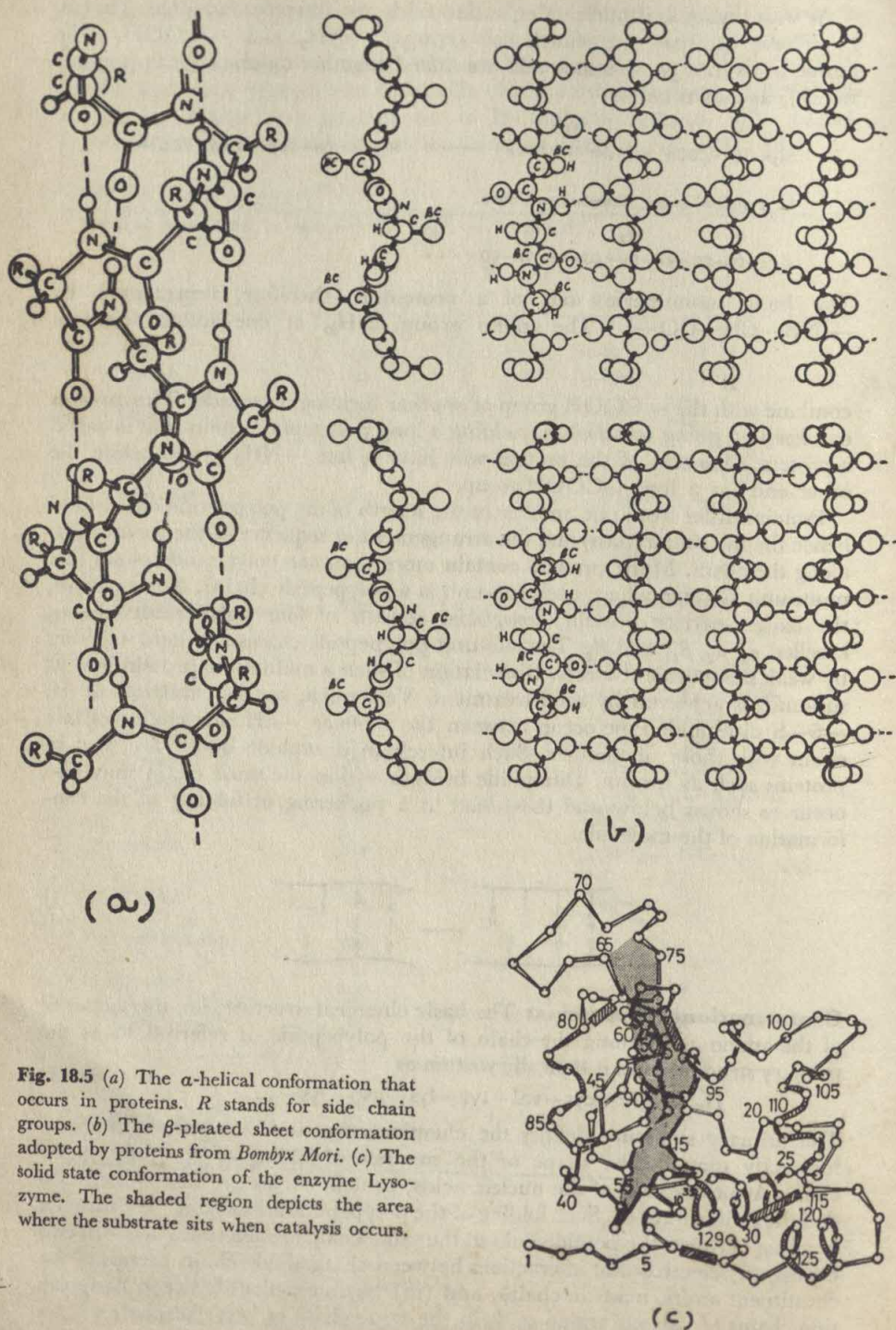
As we have seen above, many of the amino acids comprising a protein chain contain ionisable or polar side chains. These interact favourably with water in aqueous solution and aid the dissolution of the protein in water. On the other hand, nonpolar side chains like those of valine or alanine do not interact that well with water. In these cases, the solvent water finds a more favourable interaction with a more polar group, or more importantly, finds more water molecules with which hydrogen bonding is a more attractive possibility. Consequently, the nonpolar side chains tend to come together, and expel water from their vicinity. This happens to induce distant parts of the macromolecule to come together and to get 'buried' into the interior of the protein, exposing the ionic and polar group outside water medium. Such a phenomenon is termed *hydrophobic interaction.*

What shape a protein chain will undertake in the cell medium, or in its 'native' (the biologically-active) form will be governed by all the three factors mentioned above. Many proteins such as muscle proteins, (*actin* and *myosin*) and the feather protein (*keratin*), fold their chains by a regular hydrogen bonding mechanism between amide bonds in the same chain, and fold into a single chain helical array called the α-helix. The helix is held together by these hydrogen bonds as in Fig. 18.5. Certain proteins like the protein from the silkworm *Bombyx Mori*, take on the shape of a pleated sheet using two chains held together by hydrogen bonds between peptide groups of one chain with those of the other.

As opposed to these two structures which occur in what are called *fibrous proteins*, many enzymes and proteins adopt irregular conformations in solution. These irregular shapes, broadly spherical or globular in nature, arise from factors such as hydrophobic bonding, interchain disulphide linkages and ionic bonds (besides hydrogen bonding). The shape in the 'native' or biologically active state of a globular protein *lysozyme*, is shown in Fig. 18.5. The *active site*, i.e. the place where the enzyme holds the substrate is also shown in Fig. 18.5. This is an important point in the 'lock and key' fit or the specificity of enzyme action. It is believed that the conformation of the enzyme undergoes subtle changes when the substrate is bound at the active site.

In many proteins, the polypetide structure is attached to, and houses, some organic molecules known as *prosthetic groups* which impart special and specific reactivity to the protein. Some proteins also have metal ions coordinated to the amino acid side chains. Hemoglobin contains the prosthetic group called *heme*, which is a highly conjugated porphyrin molecule containing a central iron atom (Fig. 18.6). The capacity of hemoglobin to absorb, transport and release molecular oxygen from the air is due to the fact that the iron atom in heme coordinates easily and reversibly to oxygen.

Since most of the interactions that govern chain folding of proteins are weak and non-covalent, it is possible to disrupt this regular folding by physicochemical means such as heating, change in pH, addition of compounds like urea, or in some cases even cooling. Such a process leading to the disruption of the 'native' structure to yield a randomly oriented coil form is termed
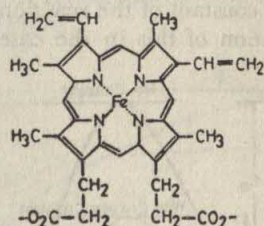
Ferroprotoporphyrin IX*
(proto)heme(IX)

Prosthetic group of
hemoglobin, myoglobin,
erythrocruorin, catalase,
peroxidase, cytochromes of class B

Fig. 18.6 The structure of the heme group—a prosthetic group occuring in many proteins

' denaturation '. Denaturation causes a loss of the protein or enzyme biological-activity.

Functions of proteins: Proteins are the major solid components of cells and serve the cell in various ways. Insoluble proteins such as collagen and proteins of hair or nails serve as structural material. Other helical proteins such as actin and myosin form part of the muscle structure and are able to absorb chemical energy and effect the contraction and relaxation of muscles. Globular proteins such as *albumin,* seen in serum plasma, regulate the water content. Many of the smaller molecular mass proteins, referred to as peptides or polypeptides, serve as *antibiotics* or *hormones.* For example, the protein *insulin* is a regulator of glucose breakdown and the cyclic peptide *gramicidin* is an anti-biotic. Proteins like *gamma globulin* are responsible for the immunity of the cell to foreign matter. Other peptides are involved in selective transport of ions. Proteins also serve as material of the cellular membranes.

Perhaps the most notable activity of a variety of proteins is their behaviour as *enzymes.* An enzyme is a protein that acts as a catalyst for a given biological reaction. For example, the enzyme *ribonuclease* catalyses the breakdown of RNA; *α-amylase* aids the hydrolysis of *α-amylose.*

18.2.4 Importance of Enzymes

Many of the reactions in cells proceed with very slow rates and with high activation energies under the conditions of cellular temperature, concentration of reactants and other conditions. And yet, these reactions have to take place in order to satisfy the metabolic, synthetic and functional needs of the cell. In order to conduct these reactions optimally, the cell utilises many globular proteins (enzymes) as catalysts.

As we have seen in Chapter 13, a catalyst facilitates the formation of products in a reaction, by decreasing the energy of activation, E_a, and thereby increasing the velocity of the reaction. In the case of reversible reactions, the catalyst speeds up both the forward and backward reactions equally; thus, the equilibrium constant of the reaction remains unaffected (see Fig. 18.7 for schematic illustration of this in the case of enzymes). After the reaction is completed, the enzyme catalyst is recovered without any loss.

Catalytic properties of enzymes in the cell are characterised by the following features: (*i*) *Specificity:* A given enzyme catalyses the conversion of a given ' substrate ' into a specific product. The enzyme *lactate dehydrogenase* catalyses the dehydrogenation of *lactic acid* to yield *pyruvic acid,* and none else. *Fumarase* catalyses the reaction of *fumaric acid* with water to yield *malic acid;* the *cis*-isomer of fumaric acid, *maleic acid,* is not catalysed. Thus, enzymatic reactions are very stereoselective. (*ii*) *Efficiency:* The conversion rate of a given substrate by an enzyme is very fast and
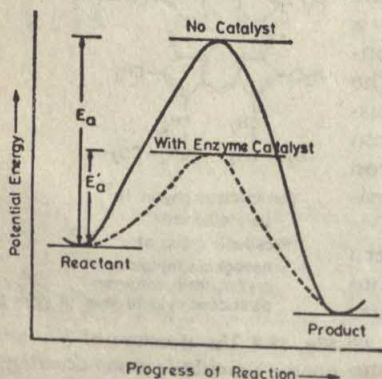
Fig 18.7 Schematic illustration of how an enzyme reduces the activation energy of a reaction from E_a to E'_a.

efficient. The rate constants may be as high as 10^6 min^{-1}; and the number of substrate molecules converted in 1 minute by one enzyme molecule are of the order of 10^2–10^6. (*iii*) *Factors affecting reactions*: In order to realise the maximum efficiency in any enzymatic reaction, the *p*H, temperature and other parameters have to be maintained at optimum values. Variation of these produces may denature the enzyme with a concurrent loss in the activity. (*iv*) *Inhibition*: In many instances, compounds that resemble the actual substrate bind to the enzyme and cause a decrease in the activity of enzymes towards the reaction.

The above mentioned factors of enzyme action can be understood on the basis of the conformational aspects, that is, the shape of the enzyme during the catalytic process. The kinetics of enzyme processes was described earlier in Chapter 13. From the plot of the reaction velocity against the substate concentration, we would get information on the maximum velocity, V_m and obtain the parameter K_m, called the Michaelis-Menten constant. The velocity of the reaction, v and also K_m are affected by temperature, ionic strength, *p*H and so on. Changes in external conditions change the degree of folding or the conformation of the enzyme, and this affects the formation of the Michaelis complex and thus the rate of the catalytic reaction. Changes in the conformation of the enzyme would thus be reflected in terms of poor efficiency, loss of specificity and reaction velocity. Correlation of enzymatic activity with enzyme conformation, therefore, forms an interesting subject of study.

Inhibition of enzyme activity can occur in two ways. Compounds that are closely related in shape and structure to the real substrate bind to the enzyme in a fashion similar to the formation of enzyme substrate; such inhibitors compete with the substrate to saturate the available site of binding on the enzyme. This is why we see in Fig. 18.8, the net effect of a *competitive inhibitor* (denoted by I) as a change in the value of K_m even though the maximal velocity is constant. This type of competitive inhibition can be overcome by increasing the concentration of the substrate; the effect is essentially one of mass action, the substrate displacing the inhibitor from the binding site. An example of competitive inhibitor is *indole*, which changes the reaction kinetics of the hydrolysis of *acetyl L-tryptophan* by the enzyme *α-chymotrypsin*.
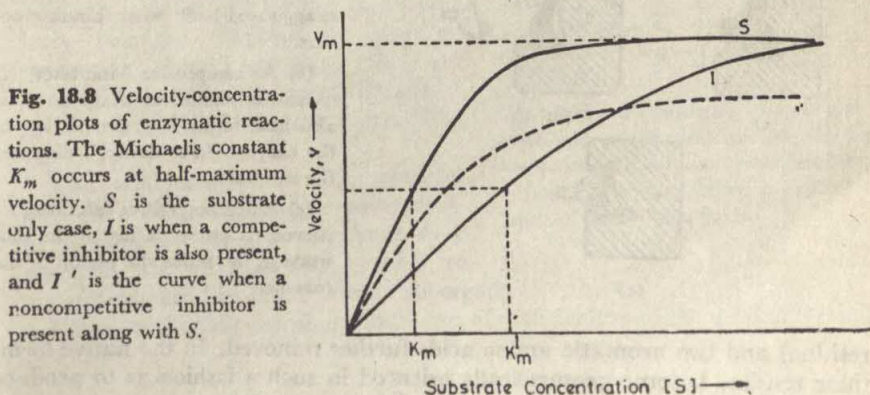
Fig. 18.8 Velocity-concentration plots of enzymatic reactions. The Michaelis constant K_m occurs at half-maximum velocity. S is the substrate only case, I is when a competitive inhibitor is also present, and I' is the curve when a noncompetitive inhibitor is present along with S.

We also have *non-competitive inhibitors* (denoted by I' in Fig. 18.8) which bind to other sites on the enzyme such as free —SH groups or even hydrogen ions as in the case of α-chymotrypsin. The EI' complex so formed is rather strong so that

simple displacement of I' by S is not effective. In the case of non-competitive inhibition, the value of K_m is not changed, but the maximal velocity V_m is reduced.

In most cases, the substrate molecule has much smaller dimensions compared to the enzyme. Consequently, only a small portion of the amino acid residues of the protein are in direct contact with the substrate, to form the enzyme-substrate complex. This, together with the specificity, inhibition and rate profiles of the catalytic process has given rise to the concept of an *active site* in the enzyme, at which the substrate is bound. The peptide and the side chain groups in the active site region are thought to be involved in a rather loose bonding with the substrate molecule. The conformation or overall chain fold-ing of the enzyme confers a specific conformation to the active site region. In this folding pattern, amino acid residues that are far away from one another may be brought in the proximity to each other forming a ' hole ' or a ' cleft ' in the enzyme architecture. The substrate molecule is supposed to fit speci-fically into this ' hole '. Only molecules with the right geometry may fit in the hole. This is the concept of the *lock-key hypothesis* proposed by Emil Fischer. The substrate that fits into the ' hole ' is clasped by the side chain groups of the amino acid residues in the active site, and the catalysed reaction occurs via normal organic chemical mechanisms. This is schematically shown in Fig. 18.9. For example, the amino acids in the active site area of lysozyme are: glu (that appears as the 35th residue from the amino end), asp (that appears as the 52nd
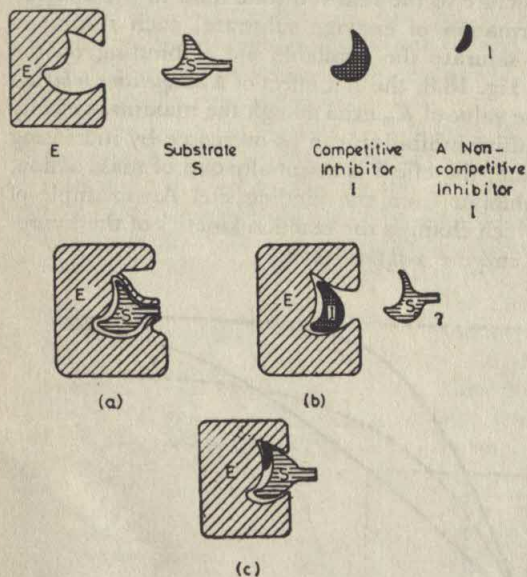
Fig. 18.9 Schematic illustration of how enzyme catalysis occurs. E is the enzyme; S the substrate, I a competitive inhibitor, and I' a noncompetitive inhibitor.

(*a*) The substrate fits into the active site of the enzyme, represented as a ' hole ' in the enzyme structure. The substrate induces an alteration in the enzyme conformation (shown greatly exaggerated here) when binding oc-curs.

(*b*) A competitive inhibitor, I, somewhat similar in shape to S, is also able to fit into the ' hole ' in the enzyme. In so doing, I displaces the substrate.

(*c*) A noncompetitive inhibitor, I', prevents a proper fitting of the sub-strate in the active site region of the enzyme.

residue) and two aromatic amino acids further removed. In the native form, these residues become geometrically oriented in such a fashion as to produce a ' hole ' that is geometrically specific for the sugar substrate.

In recent years, the idea of a rigid or a static hole or ' lock-key ' concept has been modified; rather, the substrate is thought to induce an alteration in the geometry of the active site, orienting the groups required for action. Fig. 18.9(*a*)

schematically describes the alignment of the shape of the enzyme where the substrate fits.

18.3 SMALL MOLECULES OF IMPORTANCE INSIDE THE CELL

The term *lipid* is used to denote such group of substances that dissolve readily in organic solvents but seldom in water. They are not necessarily related chemically and are generally small molecular mass substances (less than 1000). One usually includes among lipids, *fats* and *oils* (triglyceride esters of fatty acids), *phospholipids, sphingolipids, isoprenoids, steroids* and *vitamins*. The special solubility property of a lipid is exploited in the structures of cell membranes and transport of chemicals across cell walls.

$$CH_2-O-CO-R$$
$$CH-O-CO-R$$
$$CH_2-O-CO-R$$
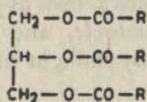
I

The fats and oils commonly encountered are the triglyceride esters of fatty acids of the general formula (I), where R is the fatty acid moiety. The common fatty acids are *stearic acid, palmitic acid,* $[CH_3(CH_2)_{14}COOH]$, *oleic acid*, and so on. Such fatty acids show ambivalence in their solubility since the polar carboxylic acid induces solubility in water because of favourable interactions with the water dipole (hydrophilic) while the long hydrocarbon tail behaves contrarily, being hydrophobic. It is this duality in behaviour that causes fatty acids to arrange themselves into regularly oriented lamellar or box-like structures termed micelles; such bimolecular lamellar arrangements afford models for biological membranes (Fig. 18.10).

Fig. 18.10 (*a*) Association of lipid molecules into a spherical micelle; (*b*) Lamellar micelle; (*c*) a schematic model of a bimolecular membrane consisting of layers of protein and lipids

The triglyceride esters of palmitic and oleic acids occur most commonly in animal and plant kingdoms and serve as reserve food supply and as ground material in limbs and other organs.

Glycerophosphatides are phosphodiesters of diglycerides of the general formula:

$$CH_2-O-CO-R$$
$$CH-O-CO-R$$
$$CH_2-O-P\underset{\underset{O}{\overset{\|}{}}}{\overset{\nearrow OH}{\searrow OX}}$$

where X is an amino alcohol. For example, *lecithin*, the phosphoglyceride, present in eggs, contains the base *choline*, $(CH_2)_3 N^+—CH_2CH_2—O^-$, as the amino alcohol. *Sphingolipids* are phosphodiesters containing the molecule *sphingosine*, and occur usually in the nerve and cerebral fluids. They have, in many cases, the phosphodiester moiety and also sugar. *Phospholipids* are usually found in cells and occur together with proteins and carbohydrates, and form part of the material of the cell membrane.
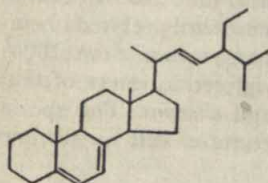
Besides fats and oils mentioned above are another important class of lipids called *steroids* (see Chapter 5). The steroid cholesterol, is found in animal tissues where it is used in the cell membranes. Correspondingly plants have the class of steroids known as *phytosterols*. Soyabean oil contains *stigmasterol:*, and yeast contains *ergosterol* which gets photochemically converted by sunlight into the steroidal *vitamin D*.

stigmasterol
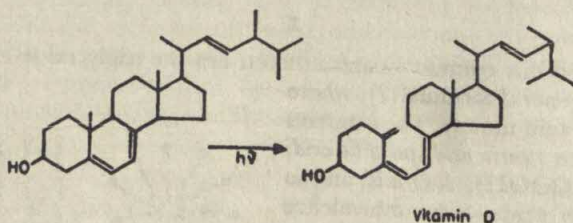
Vitamin D

Corticosteroids, found in the adrenal cortex of animals, function as hormones, stimulate glycogen formation in the liver, induce electrolyte balance and function as anti-inflammatory drugs. The female hormones,
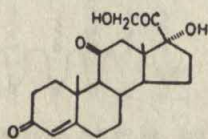
Cortisone
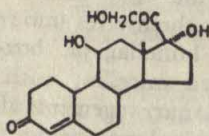
17 α hydroxy Cortisone

estrogens, formed in the ovaries, and the male sex hormones, *androgens*, are also steroids in nature.

18.3.1 Vitamins and Coenzymes

Another important class of small molecules found in living systems whose presence is essential for cellular chemical processes are the *vitamins* and *coenzymes*. The names come from the early observations that unless some of these compounds were present, enzymatic rates and metabolic processes were greatly hindered. Some vitamins like D_2 are in fact steroids, but other vitamins such as B_1 (*thiamine*) or H (*biotin*) are quite a different class of unrelated compounds.
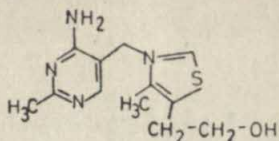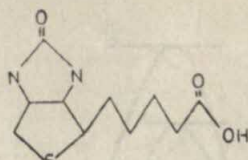
Vitamin B₁   Vitamin H

It is worth noting here that many of these vitamins are simply not synthesised in an animal's body and are thus needed as essential parts of external food eaten. Many of these vitamins are related to a series of compounds called coenzymes, which, as the name suggests, are essential for many enzymes to act.

Coenzymes are agents that mediate transfer of groups from reactants to products. They do this by acting in close concert with the enzyme. The general scheme may be illustrated as:

$$E + C \rightleftharpoons EC$$
$$EC + Ax \rightleftharpoons ECx + A$$
Subsequently, $\quad ECx + B \rightleftharpoons EC + Bx$
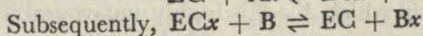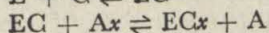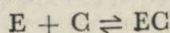
Here E is an enzyme and C a coenzyme and the net reaction is $Ax + B \rightarrow A + Bx$. For example, the coenzyme NAD^+ mediates the transfer of hydrogen from ethanol in the dehydrogenation of ethanol to acetaldehyde. The coenzyme adenosine triphosphate (ATP), is used to transfer a phosphate group in a phosphorylation reaction:

$$\text{RIBOSE} + \text{ATP} \rightarrow \text{RIBOSE-1-PHOSPHATE} + \text{ADP}$$
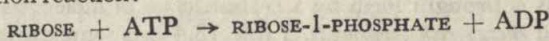
Regeneration of ATP from ADP is achieved in subsequent reactions. Such a coenzyme reaction, especially involving ATP, is very crucial in biological systems and will be discussed in section 18.3.3. Some other important coenzymes are: NAD, FAD, FMN, CoA, etc. These are used for hydrogen transfer, acyl group transfer, carboxylation, and other such functions. These compounds are the active principles and components of several vitamins.

18.3.2 Adenosine Triphosphate (ATP)

Consider a reaction like

$$\text{AMINO ACID } 1 + \text{AMINO ACID } 2 \rightarrow \text{PEPTIDE} + \Delta G$$
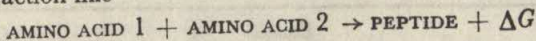
Under cellular conditions, the value of ΔG is unfavourable with the result this reaction is thermodynamically forbidden. A similar difficulty arises with the production of DNA from nucleotides or glycogen synthesis from glucose. And yet, the body or the living cell synthesises these with efficiency. The trick that the living cell uses is to convert the relevant monomers to highly 'activated' derivatives which would react, aided by the appropriate enzymes as catalysts.

Formation of the activated derivative of the monomer is equivalent to supplying the monomer with extra energy (like increasing the temperature). This charging with extra energy leads to an increase in the reactant energy levels in Fig. 18.11, which shows how an unfavourable reaction $a \rightarrow b$ can be coaxed thermodynamically to proceed with ease. One way is that the energy of the monomer can be increased by making an activated derivative of energy d; alternatively, the activation energy $(c-a)$ can be reduced by means of an enzyme catalyst (from c to e). We are concerned here with the activation of the monomer (i.e. the process $a \rightarrow d$).
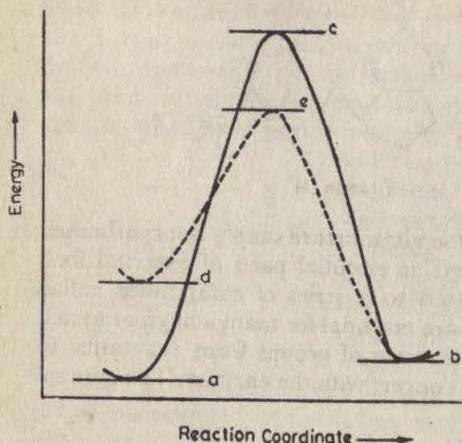
Fig. 18.11 Potential energy diagram of a reaction. (*a*: reactant; *b*: product; *c*: transition state in the uncatalysed process; *d*: 'activated' reactant; and *e*: transition state in an enzyme-catalysed process.)

Consider a set of reactions in which $X \to Y$ is highly unfavourable, but $R \to P$ is spontaneous. If these two reactions are coupled together as a combined system, the negative free energy from the RP system can be used to drive the XY system. Or, if X were somehow activated so that its energy increased from a to d (in Fig. 18.11) then conversion to the product Y (energy b) becomes thermodynamically favourable. In biological reactions, such an activation of sluggish reactants is brought forth by a certain class of molecules or cofactors collectively called *energy-rich compounds*. Table 18.4 lists some examples of such energy-rich compounds, the most common of which is the molecule adenosine triphosphate or ATP.

We define a high-energy molecule as one which releases large free energy (ΔG greater than 5 kcal mol^{-1}) upon the breaking of one bond usually by hydrolysis. For example, the reaction

$$ATP + H_2O \to ADP + \text{PHOSPHATE } (HPO^{2-}_4)$$
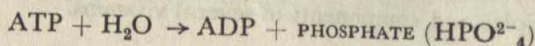
Table 18.4   High-energy Compounds

Class	Example	ΔG, kcal mol^{-1}
Nucleoside tiphosphate	Adenosine Diphosphate $ADP \rightleftharpoons AMP + HPO_4$	-6
Nucleoside triphosphate	Adenosine Triphosphate $ATP \rightleftharpoons ADP + P$	-8
Enol phosphate	Phosphoenol Pyruvate	-12
Thioesters		-8
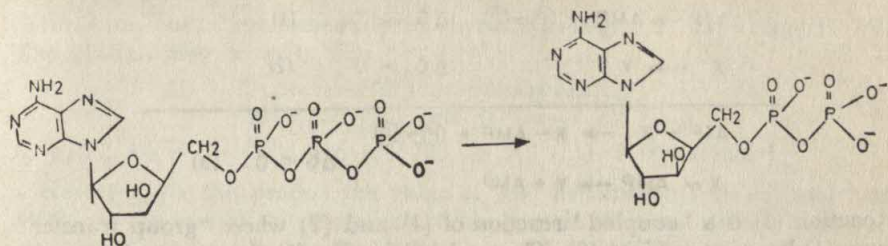
involves a ΔG change of about -8 kcal mol^{-1}. In a true sense, it is not the energy of the bond that is high, but the free energy of hydrolysis. The high energy bonds in ATP do not come from the phosphate groups *per se*, but because they are in attachment to each other and to a CH_2—O group in the molecule. Other ' active ' bonds are the pyrophosphate linkage, a phosphate bond attached to a carboxyl group (acyl phosphate) and so on. In all these cases the ' high energy ' arises not from the intrinsic energy of formation of the phosphorus–oxygen bond (about 50-70 kcal mol^{-1}), but from the free energy of transfer of a phosphate group using water as an acceptor. The free energy change for the above process is much higher ($\Delta G = -8$ kcal mol^{-1} at pH 7) than usual and hence the notion ' high energy '.

The reasons why ATP hydrolysis evolves such a large free energy are: (*i*) the high resonance energy stabilisation of the phosphates in the molecule, and (*ii*) separation of four charged-oxygens during hydrolysis releases free energy corresponding to the charge repulsion in ATP. Many reactions in the living cell require the input of free energy. The sources of such free energy are the high energy compounds like ATP. For example, the reacion

AMINO ACID 1 + AMINO ACID 2 →PEPTIDE + H_2O
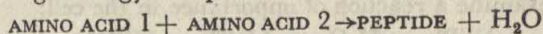
is a reaction that has a ΔG value of $+2$ kcal mol^{-1} showing that peptide synthesis needs input of energy. It is here that ATP comes in very useful. In order to aid peptide synthesis, ATP transfers its AMP group to the amino acid:
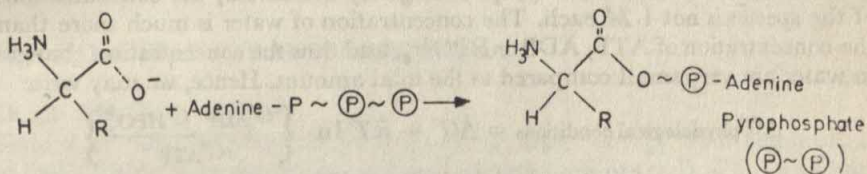
This ' activation ' involves the incorporation of a high energy bond into an amino acid, and is catalysed by a specific *amino acyl synthetase* enzyme. The activated amino acid goes on to form a peptide by reacting with a specific RNA molecule and so on, but we will come to this later. What we have shown here is that by a *coupled reaction* and a *group transfer*, ATP has activated the amino acids to proceed on towards peptide formation.

Many biological processes are the results of such ' coupled ' reactions, the first of which supplies the energy that allows the spontaneous occurrence of the second reaction. The energy supplier in these processes is ATP which itself gets degradad to ADP and phosphate. ATP may transfer its ' high energy ' to a substrate by transfer of either a phosphate group or adenyl group. It is for this reason that ATP is considered to be the energy currency in many biochemical reactions:

$$ATP \longrightarrow AMP + \text{\textcircled{P}} \sim \text{\textcircled{P}} \qquad \Delta G \ll 0 \qquad (1)$$

$$X \longrightarrow Y \qquad\qquad\qquad \Delta G > 0 \qquad (2)$$

$$ATP + X \longrightarrow X \sim AMP + \text{\textcircled{P}} \sim \text{\textcircled{P}}$$

$$X \sim AMP \longrightarrow Y + AMP \qquad\qquad \Delta G < 0 \qquad (3)$$
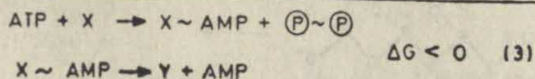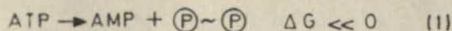
Reaction (3) is a 'coupled' reaction of (1) and (2) where 'group transfer' from (1) has occurred into (2). The total ΔG for $X \rightarrow Y$ is favourable due to the 'activation' of X by AMP.

18.4 THERMODYNAMICS IN BIOCHEMISTRY

The free energy change of a chemical reaction provides the criterion to decide whether the reaction is thermodynamically favoured or not (see Chapter 9). At equilibrium, $\Delta G = 0$ and $\Delta G° = -RT \ln K$; only when $\Delta G°$ is negative, $K > 1$ and the reaction is favoured. For example, in the following ester hydrolysis equilibrium

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$
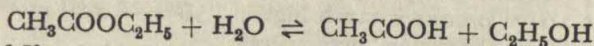
the value of K at 25°C is 18 if $[H_2O] = 1M$ and $\Delta G° = -1710$ cal mol^{-1}. The reaction is favoured and hydrolysis of the ester will occur. If the reaction were carried out in water solution, $[H_2O] = 55\ M$ (1 litre of water $= 55\ M$ of water), then the free energy change becomes $+650$ cal mol^{-1} and we see that the reaction becomes unfavourable. Thus, the concentrations of the species are important.

Let us now examine a reaction of importance in the cell:

$$ATP^{4-} + H_2O \rightleftharpoons ADP^{2-} + HPO^{2-}_4$$
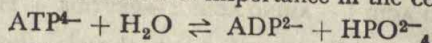
Under standard conditions (i.e. when the concentrations of all the species is $1M$), $\Delta G° = -7000$ cal mol^{-1}. The reaction is highly spontaneous. However, we know that under cellular (or physiological) conditions, the concentrations of the species is not $1\ M$ each. The concentration of water is much more than the concentration of ATP, ADP or HPO$^{2-}_4$, and thus the concentration changes in water are very small compared to the total amount. Hence, we may write

$$\Delta G'_{\text{physiological conditions}} = \Delta G° + RT \ln \left\{ \frac{C'_{ADP}\ C'_{HPO_4^{2-}}}{C'_{ATP}} \right\}$$

where the prime refers to physiological condition. In general, in the cell, $C'_{HPO^{2-}_4} \ll 1\ M$ and also $C'_{ADP} = C'_{ATP}$.

If we take $C_{HPO_4} \simeq 0.1\ M$, then at 37°C,

$$\Delta G' = -7000 + 2 \times 310K \times 2.303 \log 10^{-1}$$
$$\simeq -7000 - 1400 \simeq -8400 \text{ cal mol}^{-1}$$

Thus, the value of ΔG for the hydrolysis of ATP at physiological concentrations is significantly more favoured than at the standard conditions.

As an example of physical variables affecting the direction of a process, let us look at the denaturation of a protein. The native chain conformation of *chymotrypsinogen*, a globular protein, is governed by hydrogen bonding, ionic interactions and hydrophobic forces. If these interactions are weakened or broken by some means, such as heat, the protein chain opens up from the compact shape to a more random structure. This phenomenon known as de-

naturation, occurs spontaneously in chymotrypsinogen at 43°C and pH 1·7. The process may be written as

$$\text{NATIVE } (\mathcal{N}) \rightleftharpoons \text{DENATURED } (D)$$
$$K = [D]/[\mathcal{N}] \text{ and } \Delta G^\circ = - RT \ln K$$
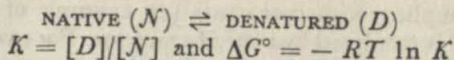
At 43°C, $\Delta G^\circ = - (2 \times 316 \times 2\cdot703 \log K) = - 1000 \text{ cal mol}^{-1}$

However, for this process the value of ΔG° becomes $+1000$ cal mol^{-1} at 34°C; we see that at this temperature, the protein does not denature spontaneously. Near the physiological temperature, (say, 38°C), $\Delta G^\circ = 0$, i.e. an equilibrium is established at unit concentrations of the denatured and active forms. Of course, if $[D] \neq 1$ and $[\mathcal{N}] \neq 1$ mol litre^{-1}, ΔG may well differ from 0 at 38°C.

In the case of two reactions, one of which is highly favourable but the other is accompanied by a positive ΔG, it is possible to couple the reactions in such a way that the first reaction drives the second to completion. Consider

$$\overset{\text{Mg}^{+2}}{\text{ATP} + \text{H}_2\text{O} \rightleftharpoons \text{ADP} + \text{P}_i} \quad \Delta G^\circ_1 = - 7400 \text{ cal mol}^{-1}, K_1 > 1 \quad (1)$$

$$\text{GLUTAMATE} + \text{NH}^+_4 \rightleftharpoons \text{GLUTAMINE} \quad \Delta G^\circ_2 = + 3750 \text{ cal mol}^{-1}, K_2 < 1 \quad (2)$$
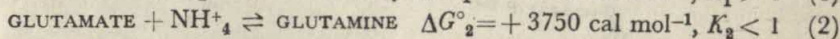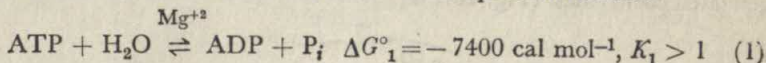
If we combine the reactions, as happens in the cell,

$$\overset{\text{Mg}^+}{\text{ATP} + \text{GLUTAMATE} + \text{NH}^+_4 + \text{H}_2\text{O} \rightleftharpoons \text{ADP} + \text{GLUTAMINE} + \text{P}i} \quad (3)$$
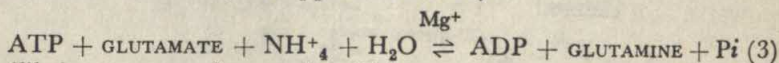
The equilibrium constant for reaction (3) is

$$K = \frac{[\text{GLUTAMINE}] \ [\text{ADP}] \ [\text{P}_i]}{[\text{GLUTAMATE}] \ [\text{ATP}] \ [\text{NH}^+_4]}$$
$$= K_2 \cdot K_1$$

and $\Delta G_3^\circ = -RT \ln (K_2 K_1) = \Delta G_1^\circ + \Delta G_2^\circ = -3650 \text{ cal mol}^{-1}$. This spontaneity is imparted to reaction (3) by the ATP hydrolysis. Many biological reactions tend to become favourable by utilising this principle of coupled reactions.

18.5 HOW CELLS TRANSFORM ENERGY

18.5.1 The Fate of Food

Similar to other engines, the cell derives its input energy from combustion of fuel (arising from the chemical bonds of molecules of food). Thus, the best food molecules are those that liberate large amounts of free energy and are thermodynamically unstable. Glucose, for example, is an excellent food molecule since it is easily oxidised; upon complete oxidation to carbon dioxide and water in the laboratory, it yields 690 kcalories mol^{-1} of heat. But the temperatures required for this combustion are much higher than the physiological temperature of 37°C. Hence the cell degrades the glucose molecule in stages, all at this low temperature and in dilute solution, and utilises the free energy liberated in the breakdown of glucose for the formation of ' high energy ' molecules such as ATP.

The process of degrading a food molecule to eventually produce cellular building blocks is termed *intermediary metabolism*. The breakdown of a food molecule usually involves oxidising it to its ultimate products.

$$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{ENERGY}$$
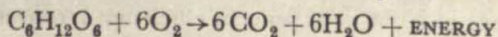
Biological oxidation is both *aerobic* (i.e. in presence of air) and *anerobic* (no air). Anerobic oxidation is, in fact, dehydrogenation. This dehydrogenation usually occurs through coupling with coenzymes (an example of which, NAD+, was shown earlier) and is catalysed by a specific enzyme. For example, the oxidation of lactate to pyruvate is coupled and mediated by the coenzyme NAD, which receives two hydrogen atoms from the lactate. The reaction is catalysed by the enzyme-lactate dehydrogenase (LDH). Sometimes, this dehydrogenation may

$$
\begin{array}{ccc}
COO^- & & COO^- \\
| & & | \\
H-C-OH & + NAD \xrightarrow{LDH} & C=O & + NADH_2 \\
| & & | \\
CH_3 & & CH_3
\end{array}
$$
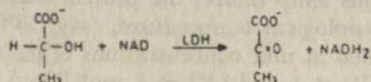
occur via a relay process where the hydrogen atoms are relayed from one coenzyme to another. In a series of such oxidation-reduction steps, oxygen may not be immediately necessary, but participates indirectly to oxidise the dehydrogeneated coenzymes. (Fig. 18.13b).
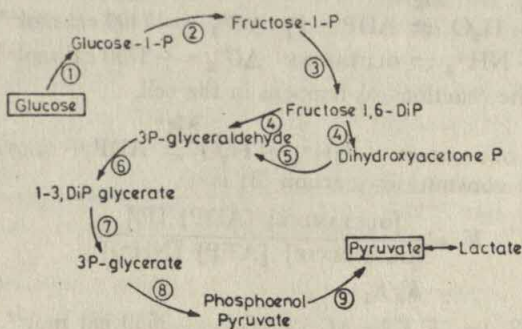
The Embden - Meyerhof pathway

Net reaction :

Glucose ⟶ 2 Pyruvate + 2 ATP

Fig. 18.12 Glucose metabolism. In the anerobic stage glucose is broken down to pyruvate. See text for details.

A food molecule is metabolised in the cell for the dual purpose of synthesising necessary compounds for cellular construction and function, and for storing energy in the form of ATP that may be used in processes such as contraction of muscles, driving unfavourable reactions and so on. In Figs. 18.12 and 18.13 we briefly summarise the metabolism of glucose in a living cell. Notice that each step is catalysed by a specific enzyme. ATP is used to drive steps 1 and 3, while steps 7 and 9 regenerate ATP, leading to a net production of two ATP molecules along with two pyruvates. Thus, one mole of glucose, in the absence of air so far, has been broken down to produce two moles of a 3-carbon molecule *pyruvate* (or *lactate*) and the net free energy stored in this nine-step degradation is roughly 20 kcal mol⁻¹ (for synthesis of two ATP molecules). Since the energy released in converting glucose to lactic acid is 56 kcal mol⁻¹ we see that the cell has an efficiency of 20/56 or 35 per cent efficiency in converting heat energy

(a)

Pyruvate

Acetyl Co-A

Oxalo acetic

Citric

Malic

Cis-aconitic

Fumaric

Succinic

Isocitric

Succinyl Co-A

Oxalosuccinic

α-keto glutaric

(b)

TCA cycle

NADH$_2$ → FADH$_2$ → Co-QH$_2$ → 2Fe^{2+} → H$_2$O

NAD → FAD → Co-Q → 2Fe^{3+} → O$_2$

ADP → ATP   ADP → ATP
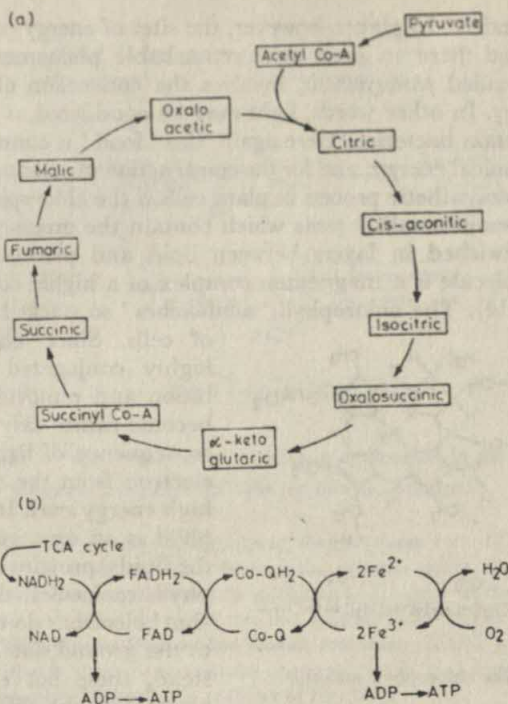
Fig. 18.13 (*a*) The tricarboxylic acid cycle and (*b*) the respiratory chain of reactions

to chemical energy in terms of ATP. The breakdown of lactate (or pyruvate) to carbon dioxide and water occurs through the *tricarboxylic acid cycle* (the *Krebs cycle*) and the respiratory chain reactions, as shown in Fig. 18.13. This reaction series occurs in presence of oxygen (aerobic) and it is in these steps that the major portion of energy is captured. First the lactate is converted into an activated form of acetic acid called *Acetyl Co*-A which reacts with members of the Krebs cycle. The three carbons of pyruvic acid are oxidised to carbon dioxide. In the course of the cycle, electrons are extracted from the intermediates by specific enzymes and fed into a series of electron-carrier molecules collectively called the *respiratory chain*. At the last link, the electrons combine with oxygen to yield water. It is in this aerobic series that maximum energy transduction occurs. For every lactate, the cell produces eighteen molecules of ATP, and thus from one glucose molecule, the total amount of ATP produced is thirty-eight, two from the anerobic metabolism of glucose to two lactates and eighteen from each lactate. If one roughly estimates each ATP to release 10 kcal mol^{-1} as available free energy, this adds up to 380 kcal mol^{-1} of glucose that is saved and stored via the metabolic pathway in the cell. This points to an efficiency of about 50 per cent for the cell as a machine.

18.5.2 Photosynthesis
It is worthwhile remembering here that the glucose metabolism occurs in cells

in the mitochondria. In plants, however, the sites of energy conversion are the chloroplasts, and there an even more remarkable phenomenon occurs. This phenomenon, called *photosynthesis*, involves the conversion of light energy to chemical energy. In other words, light may be considered as ' food ' for green plants (and certain bacteria). Here again, this ' food ' is consumed in the cells to produce chemical energy, and for the construction of cellular building blocks. The site of photosynthetic process in plant cells is the chloroplast. Each chloroplast contains entities called *grana* which contain the green-coloured pigment *chlorophyll* sandwiched in layers between lipid and protein molecules. The chlorophyll molecule is a magnesium complex of a highly conjugated heterocycle (Fig. 18.14). The chlorophyll ' sandwiches ' so stacked act as a battery of cells. Since chlorophyll has a highly conjugated structure, excitation and removal of an electron become rather easy. The immediate consequence of light is to excite an electron from the chlorophyll to a high energy level. In the cell, chlorophyll is so arranged spatially with the lipids, proteins and other chlorophyll molecules that the excited ' hot ' electrons do not simply return to the ground state, as expected. Instead, these hot electrons are led away from the chlorophyll molecule
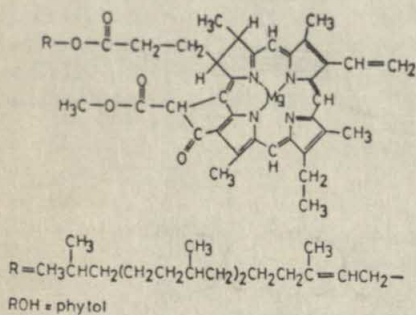
$R = CH_3CHCH_2(CH_2CH_2CHCH_2)_2CH_2CH_2C = CHCH_2-$

ROH = phytol

Fig. 18.14 The chlorophyll molecule

by associated electron-carrier molecules (called *cofactors*) and handed from one to another around a circular chain of reactions. During this relay, the energy of the electrons is taken up in steps towards producing energy-rich ATP molecules. The electron which has thus transferred its energy may either return to a chlorophyll molecule (thus completing the path of *cyclic photophosphorylation*) or may be taken up by the cofactor NADP (*non-cyclic photophosphorylation*).

It is interesting to see that the chlorophyll molecule in the laboratory cannot store or utilise the energy of the photon; the energy is immediately discharged. It is the spatial arrangement of the chlorophyll and its proximal orientation to the lipids, cofactors, and proteins that make it active in the cell. The primary process in photosynthesis and the schematic mechanics of production of glucose are outlined in Figs. 18.15 and 18.16.
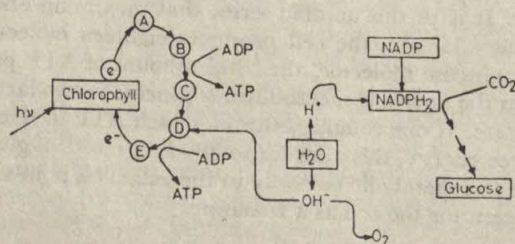
Fig. 18.15 ' The light reaction ' in photosynthesis illustrating the cyclic and the noncyclic photophosphorylation

Net Reaction : $6 CO_2 + 6 H_2O \longrightarrow C_6H_{12}O_6$
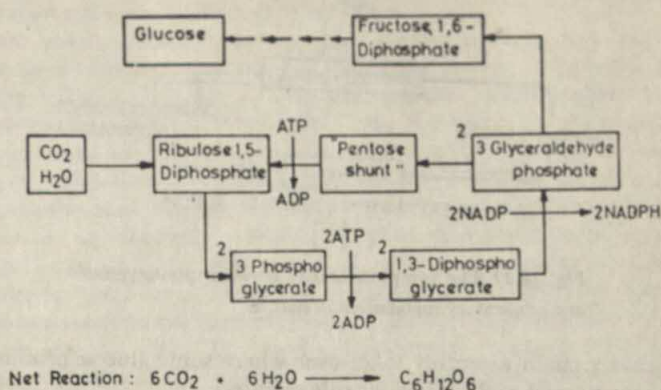
Fig. 18.16 In ' the dark reaction ' glucose is synthesised in the second stage of photosynthesis, after the light reaction has occurred

The scheme $A \to E$ cycle is the cyclic pathway that produces two *ATP* molecules, while the other route utilises the cofactor NADP. Water is the external source of electrons here. The OH yields oxygen and electrons that return to chlorophyll, while in the process one ATP molecule is also produced. Here, the 'light' reaction is until NADP has captured an electron. In order to biosynthesise glucose from carbon dioxide and water, NADP goes through a series of 'dark' reactions (that is, these do not require photons). Notice that several of the steps here are reversal of the glycolytic degradation pathway of Fig. 18.12.

Synthesis of glucose from carbon dioxide and water is a ' dark ' reaction, which means that it involves a series of reactions that do not directly require light. The two components needed are ATP and $NADPH_2$, both made as a result of ' light ' reactions. ATP is the energy supply and the cofactor $NADPH_2$ is the reducing agent. In the cycle for the synthesis of glucose shown above, the key intermediate is *ribulose* 1, *5-diphosphate*, which combines with CO_2 to produce 3 *phosphoglycerate*. In the series of steps leading from phosphoglycerate to glucose, ATP and $NADPH_2$ are used up. Meanwhile, the key intermediate ribulose 1, 5-diphosphate is regenerated from 3- *glyceraldehyde phosphate* via a series of reactions collectively termed the *pentose shunt*.

The photosynthetic assembly in plant greens may be viewed as a miniature solar power plant, since it uses the sun's light directly to convert it to chemical energy in the form of ATP and glucose. The efficiency of the photosynthetic assembly under selected laboratory conditions reaches as high as 75 per cent, i.e. three quarters of the input light energy is converted to chemical energy. This is, of course, quite different from natural conditions and thus may be an upper limit.

It is interesting to note the complementarity of the two processes, photosynthesis and respiration. The former converts inorganic oxides such as carbon dioxide and water photochemically to molecules of energy and food, and releases oxygen. Respiration involves the uptake of oxygen by plants and animals, and oxidation of molecules of food to produce inorganic oxides and biologically useful energy. Together these two processes drive the cyclic flow of matter and flow of energy through the *eco-system*, or the *biosphere* (Fig. 18.17).

Green plants go through the above complementary cycle on a daily schedule. During daytime, solar energy is used for photosynthesis and glucose synthesis occurs and the plant gives out oxygen. After sunset, photosynthesis ceases and
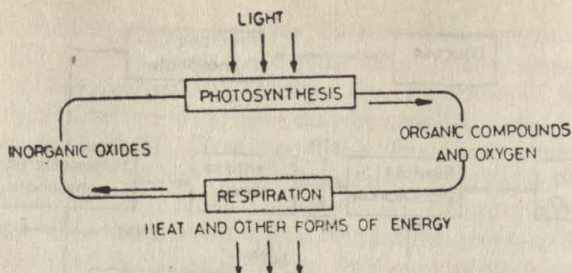
Fig. 18.17 The complementarity between photosynthesis
and respiratory metabolism in nature

the respiratory chain assembly takes over where some glucose produced in the
daytime is consumed and carbon dioxide released.

18.5.3 Oxidation-reduction Equilibria

The involvement of coenzymes such as NAD, FAD and FMN in metabolic and
energy-capturing schemes was explained earlier. In the respiratory cycle,
oxygen gets reduced to water, but the reduction occurs through a series of steps
each of which involves the transfer of one electron from coenzyme to coenzyme.
The heme proteins, *cytochromes*, are some of the important electron carriers. In
fact, the statement has been made that all redox reactions in biology occur
through one electron-transfer. In many processes, the release (or uptake) of
energy may not occur as thermal energy, but as electrical energy in terms of
the electrical potential. The relation between the electrical potential involved
in the process and the free energy is given by the equation, $\Delta G° = -nFE°$
where $E°$ is the electrical potential and F the Faraday constant equal to
96,500 coulombs ($=23,000$ cal volt^{-1}) and n the number of electrons involved
in the process. And the redox reaction of A will not happen if $E < 0$
(i.e. $\Delta G > 0$).

In the oxidation of pyruvate through the citric acid cycle, (Fig. 18.13), several
coenzymes are involved, notably NAD. In several steps of the cycle, NAD gets
reduced to $NADH_2$. Regeneration of the oxidised form, NAD, is achieved by
oxygen through the respiratory assembly. Here again, the process is a series of
one-electron transfers mediated by coenzymes and cytochrome proteins (see
Fig. 18.13*b*).

Thermodynamically one may write this as

$$2\,NADH + \tfrac{1}{2}\,O_2 \rightleftharpoons 2\,NAD + H_2O$$
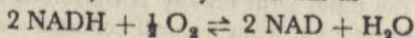
The electromotive force, $E°$, at standard state for the NADH $\rightarrow$ NAD oxidation
is -0.32 V and for the reduction of $O_2 \rightarrow H_2O$ is $+0.81$ V. When these two half-
reactions are combined, the total $E°$ for the reaction is $+0.81 -(-0.32)$ V
$=1.13$ V and the oxidation of NADH by oxygen is a highly favoured process.
The corresponding free energy of oxidation $\Delta G° = -(1.13 \times 23000 \times 2) = -52$
kcal mol^{-1}. About 60 per cent of this energy is used to produce three moles of
ATP from ADP:

$$2\,NADH + 2H^+ + O_2 + 3\,ADP + 3\;\text{PHOSPHATE} \rightleftharpoons$$

$$2\,NAD + 3\,ATP + 2\,H_2O$$
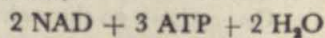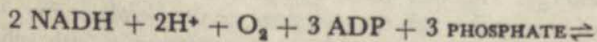
This process is referred to as *oxidative phosphorylation*.

18.5.4 Biosynthesis of Small Molecules

We have briefly looked at the pathways by which living cells transform input energy, be it food molecules or other forms of energy, into useful free energy. A glance at Figs. 18.12 and 18.13 tells us, however, that in order for this machinery to function, the cell needs molecules like enzymes, coenzymes, phospho compounds and sulphur compounds. There ought to be ways by which the cell makes or replenishes these essential molecules. Since the input fuel of the cell is used for the dual purpose of storing useful free energy and making molecules essential for its function, it should be clear that the metabolic pathways in Figs. 18.12 and 18.13 are only partial, and that there should exist metabolic and biosynthetic routes for amino acids, nucleotides, and cofactors. The cell for its growth and function requires nitrogen, sulphur, phosphorus and trace amounts of metals such as Mg^{2+}. The food requirements, or the nutrient medium for growth, of mammalian cells are complex, while the growth medium for a bacterium such as E. coli is indeed very modest. A simple synthetic growth medium for E. coli is shown in Table 18.5. With this nutritional medium, E. coli cells grow and reproduce within an hour at 37°C. If this simple starvation diet were supplemented by the addition of amino acids, purines and pyrimidines, the growth is more rapid and the generation time is only 20 minutes. It is easy to see on the basis of the diet and the metabolic route (Fig. 18.12) how the E. coli cells would transform the glucose. E. coli cells can, however, be grown, although a little less efficiently, on a diet where glucose in Table 18.5 is replaced by any simple amino acid like glycine or leucine. The metabolic machinery still goes on! This means that (i) when glucose is the sole carbon source, all the amino acids, nucleotides and other molecules needed for E. coli growth must be derived from metabolites derived from glucose and (ii) when amino acids are the source of carbon rather than sugar, normal growth still occurs. Therefore, there must also exist twenty routes of amino acid metabolism by which key metabolites are produced in the E. coli cells. Such degradative pathways also exist for lipids, nucleotides and fats.

Based on the above statements, a unified picture for the utilisation of the input fuel in the E. coli cells emerges. Fig. 18.18 illustrates in a comprehensive fashion how the E. coli cell utilises glucose to produce useful energy like ATP and to synthesise amino acids, nucleotides, fats and sugars. From these basic monomers, synthesis of polymers such as enzymes, nucleic acids and polyglycans occurs in the cell.

Table 18.5   A Simple Growth Medium for E. coli Cells

NH_4Cl	1·0	g
$MgSO_4$	0·13	g
KH_2PO_4	3·0	g
Na_2HPO_4	6·0	g
Glucose	4·0	g
Water	1000·0	ml
Other ions	traces	
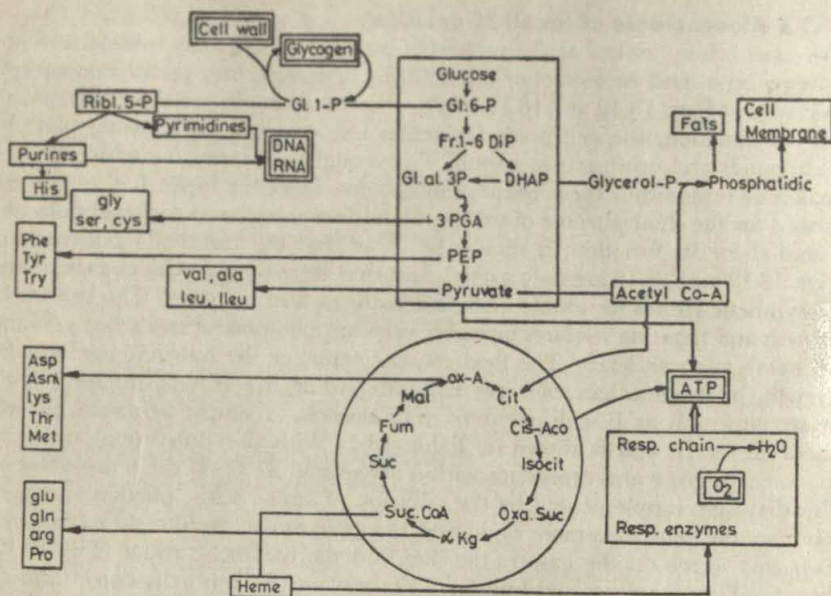
Fig. 18.18 The basic metabolic and biosynthetic pathways of E. coli

We have shown how the cell has developed its main metabolic and biosynthetic pathways, starting from glucose as its primary carbon source. Alternate schemes of metabolism using other carbon sources are also built in the scheme, as illustrated in Fig. 18.18. Yet, this is not the complete story. Besides glucose (carbon source) the cell needs of external supply of nitrogen (NH_4Cl), phosphorus (KH_2PO_4, Na_2HPO_4), sulphur (Na_2SO_4), and other elements. It is interesting to see how some of these elements are taken (incorporated) into the cell.

There exist, in nature, special kinds of bacteria such as *azotobacter* that assimilate atmospheric nitrogen. Symbiotic systems comprising the bacterium *rhizobium* and the leguminous plants also fix nitrogen. Reduction of nitrogen to ammonia occurs here aided by the pyruvic acid metabolism and an electron-carrier protein called *ferridoxin*. Other cells are able to take nitrate as the nitrogen soure and reduce it to NH_3 or NH_4^+. As we saw, the nitrogen soure of E. coli is NH_4Cl. One way the nitrogen is incorporated in the E. coli scheme is to react α-ketoglutaric acid with NH_4^+ and produce glutamic acid. (Another scheme is to fix CO_2 and NH_4^+ with ATP to produce *carbanoyl phosphate*, a high-energy compound.) In lower organisms, sulphate, (sulphur source) can react with ATP, forming a high-energy system allowing it to form sulphate esters. Likewise, inorganic phosphate is also incorporated directly into high energy phosphate esters, as seen by the fact that in order for yeast to ferment alcohol, phosphate is essential.

18.5.5 Nutrition

The nutritional needs of a low organism such as E. coli are illustrated in Table 18.5. When we turn to higher systems such as mammalians and man, we notice that many of the biosynthetic pathways of Fig. 18.18 are simply not available. Man does not possess the biochemical versatility of the bug with the result his nutritional needs for normal growth are more stringent. For example, in the evolutionary scheme, he has lost the synthetic apparatus to produce amino acids such as *leucine, isoleucine, valine, lysine, methionine, phenylalanine, threonine* and *tyrosine*. These amino acids have to form part of the food he eats as proteins (meat, peas, milk,) and these are termed *essential amino acids*. Likewise, he has no

Table 18.6 Recommended Daily Nutritional Requirements for Proper Growth

Protein	Ca²⁺	Fe²⁺	Vitamin A	Thiamine	Ribo-flavin	Nicotinic acid	Vitamin C	Vitamin D
			18-*year old boy* (Total calories required 3000 per day)					
85 g	1·0 g	20 mg	5000 units	1·8 mg	1·9 mg	18 mg	50 mg	400 units
			18-*year old girl* (Total calories required 2500 per day)					
80 g	1·0 g	20 mg	5000 units	1·4 mg	1·5 mg	14 mg	50 mg	400 units

ability to biosynthesise many coenzymes. These again form part of his essential nutritional needs, in the form of vitamins. Trace metal ions also are nutritional requirements for normal growth. Many organic disorders, diseases and malfunctions in man are directly traceable to a want of these essential metabolites. Many disorders that arise out of a deficiency of, say vitamins, can be rectified upon administration of the required chemicals. The recommended daily nutritional needs for the human body are listed in Table 18.6.

18.6 BIOSYNTHESIS OF MACROMOLECULES

The pathways for the synthesis of amino acids, nucleotides, and sugars are illustrated in Fig. 18.18. Synthesis of the appropriate macromolecules in the cell occurs by means of polymerisation reactions. The macromolecules of interest are polysaccharides, proteins, RNA, and DNA. Polysaccharides such as starch or glycogen are used as structural material or as food and do not carry any information or codes for metabolism or regulation. On the other hand, proteins and nucleic acids carry information in the sequence of the monomers along the chain. The amino acid sequence of an enzyme determines its chain architecture and also what kind of an enzyme it would be. The base sequence of a DNA molecule has stored in it the information for the synthesis of a given enzyme. Thus, the biological properties of a nucleic acid or a protein are dictated by *information-carrying sequences* of the monomeric units. Such an information content is not built into the polysaccharides. Consequently, the method and mechanism of synthesis of a polysugar is essentially the same as that of small molecules, while biosynthesis of proteins and nucleic acids are a little more involved. We shall briefly examine the biosynthesis of nucleic acids and proteins in this section.

18.6.1 Biosynthesis of DNA: The Genetic Code
When we get to a study of the synthesis of nucleic acids and proteins, we are in essence studying the molecular basis of life. During cell division, reproduction, or more precisely, duplication of the nuclear material occurs. From then on, a complete duplication of the cell occurs with great precision and fidelity, such that the 'daughter' cell formed is identical in totality with the parent. All the information required for the cell division is encased in its nuclear matter, the chromosome. The chromosome contains the information, or the code, for its duplication and also for the production of proteins, enzymes and other chemicals required for the growth and functions of the cell. The main constituent of the

chromosome is DNA and thus we are led to the conclusion that the DNA molecule in the cell nucleus is the ' master ' molecule that possesses the ' *genetic code* '.

We know from genetics that chromosomes contain the hereditary properties of all cells and this information is stored in specific regions called *genes*. Genes control a cell's protein production, and thus its metabolic functions. Thus there exists a direct correlation between a gene and a specific protein that is synthesised in the cell cytoplasm. Extensive studies have shown that the chromosomal molecule is DNA and that genes are in fact portions or regions of the
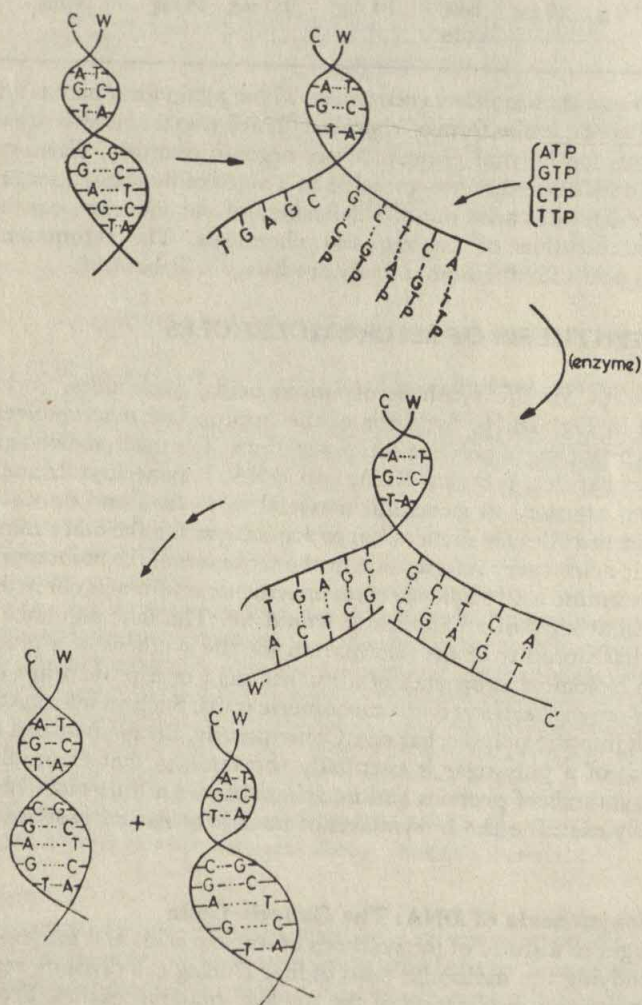
Fig. 18.19 Biosynthesis of DNA. A ' parent' DNA molecule with the strands denoted as C and W acts as the template. The strands unwind. Strands of the ' daughter ' DNA molecule are synthesised. C' is synthesised on template W, and W' synthesised on template C. After complete stands are synthesised, we obtain a ' semiconservative ' duplication of DNA. The new molecules are $C'W$ and CW'.

DNA polymeric chain. The chromosome of E. coli cells is one DNA molecule of molecular mass about 10^9 and has the code for about 10^3 genes. This means that each gene has a molecular mass of about 10^6. Put in another way, the E. Coli chromosomal DNA has about 1.5×10^6 monomers along the chains and each gene is a region corresponding to 1500 residues in this DNA. We shall now examine the two important aspects of biosynthesis—chromosome duplication and gene-directed protein production. In molecular terms, these problems can be translated as (*i*) how does the DNA duplicate itself and (*ii*) how does it control the production of proteins in the cell?

As described earlier, DNA is a polymer with repeating nucleotide monomers linked to each other by means of phosphate bonds (see section 18.2.2 and Fig. 18.4). Each DNA molecule is characterised by its chain length and by the sequence of the heterocyclic bases (*A, G, C, T*) along the chain as we proceed from one end (3' of the sugar, deoxyribose) to the other (5' end). In addition, the conformation of DNA is a double helix in which two DNA chains are held together through hydrogen bonds specifically between *A* and *T* as well as between *G* and *C*. Because of this base-pairing complementarity, if the sequence of one chain (strand) is known, that of the other is automatically fixed. In other words, we may suggest that one strand acts as the mould or *template* for the other. Or, it is possible to (*i*) align monomeric nucleotides in a complementary fashion along a given strand of DNA template and (*ii*) to form covalent phosphate bonds between the aligned monomers and thereby synthesise a new DNA strand on the template. It is, in fact, exactly in this ingenious fashion that new DNA molecules are made in the cell. The new DNA molecules are exact copies of the parent DNA as a result of the template synthesis. This affords the molecular mechanism of gene replication. A schematic illustration of the template duplication of DNA molecules is depicted in Fig. 18.19. In the first stage, the parent DNA double helix unwinds exposing the two template strands. The exact forces or conditions under which such a separation of strands occurs is still not clear.

In the second stage, the monomeric deoxy-nucleotides GTP, ATP, CTP and TTP enter the nucleus of the cell and align themselves appropriately on the template strands. Once the nucleotides are aligned appropriately, phosphodiester bonds are formed between the neighbouring monomers, catalysed by an enzyme termed *DNA polymerase*. One strand of the parent DNA acts as the template for synthesising the complementary strand of a daughter DNA. After the daughter strand is completely synthesised, it pairs off with the parent template to yield a double stranded DNA that is an exact copy of the original.

18.6.2 Biosynthesis of RNA and Proteins

The biosynthesis of proteins in the cell occurs not in the nucleus but in ribosomes (in the cytoplasm). The code for the process responsible for this synthesis is contained in the genes (or in the sequence of bases along the DNA chain residing in the nucleus). Hence, there must be a mechanism for (*i*) transmitting the information or a messenger system that carries the genetic code from the nuclear DNA to the ribosomal site where proteins are mades, (*ii*) the transfer of the appropriate amino acids in sequence to the ribosomal site, and (*iii*) proper binding and orientation of the molecules at the ribosome whereby the message from the nuclear DNA is translated properly into the protein synthesis. It is known that messenger RNA or *m*-RNA is involved in carrying the genetic

code from the nucleus to ribosome. Twenty different *t*-RNA molecules are known to occur in the cell, each of which specifically binds to a specific amino acid and takes the amino acid to the ribosome. Ribosomal RNA or *r*-RNA is known to form part of the ribosomal matter where it provides a means of aligning *m*-RNA on the ribosome and letting it interact with *t*-RNA. As seen before, the chemical structures of RNA and DNA are quite similar. While RNA has ribose on the sugar moiety, DNA has 2-deoxyribose; the base uracil (U) that appears in RNA is replaced by thymine (T) in DNA. The base pairing complementarity is the same in the two, i.e. G pairs up with C and A with T (in DNA) or U (in RNA). With this similarity, it is tempting to propose that the synthesis of RNA occurs in much the same way as DNA strand duplication. This proposal has in fact been verified to be valid. RNA synthesis occurs in the nucleus using the unwinding strand of DNA as template. The appropriate ribonucleotide phosphates enter the nucleus, pair up complementarily with the sequence of bases of the DNA as illustrated in Fig. 18.19 and an enzyme called *RNA polymerase* mediates the covalent linkage between the ribo-nucleotides to produce RNA. The base sequence of the biosynthesised RNA is complementary to that of the DNA strand template. While for DNA duplication both strands of DNA act as templates, for RNA synthesis only one strand acts as a template. This RNA that is synthesised in the nucleus as a transcript of the genetic code of DNA, is the messenger RNA and is found to pass on from the nucleus to the ribosomal site. The base sequence of *m*-RNA is 1500 nucleotides long or roughly the length of one gene. Thus for every gene, one *m*-RNA is produced.

The other two types of RNA (i.e. *r*-RNA and *t*-RNA) are also synthesised from the DNA. The *r*-RNA is of very high molecular mass and is found as a constituent of ribosomes, and *t*-RNA seen in the cytoplasm is about 80 units long and is seen to concentrate around the ribosome during protein synthesis.

When we turn to the question of the biosynthesis of proteins, we need to consider the energetics of peptide bond formation and also the alignment of the proper amino acids in sequence to form the protein. The energy required for peptide bond formation is given to the amino acid by 'activation'. Each amino acid, so activated, complexes with a specific *t*-RNA, and the aminoacyl-*t*-RNA then travels to the ribosome. For each of the twenty amino acids that constitute a protein there is a specific *t*-RNA, making a total of twenty *t*-RNAs.

The *m*-RNA that is synthesised in the nucleus, as a transcript of the information contained in the gene (in the form of base sequence) comes out of the nucleus and attaches itself to the ribosomes (*r*-RNA); several such ribosomes attach to a *m*-RNA and form the active ' polysome' where protein synthesis occurs. In general, the genetic message or the protein code in *m*-RNA may code for as many as 500 amino acids in a protein chain. The ' code ' for each amino acid is a sequence of three bases along the DNA and hence the *m*-RNA chain. For example, a specific sequence of say ...*AAA*... in the DNA will be transcribed in the *m*-RNA as ...*UUU*... and this three letter code is specific for the incorporation of the amino acid phenylalanine in a growing protein chain in the polysome. The triplet code TAG in the DNA will be transcribed in the *m*-RNA as AUC and will incorporate the amino acid isoleucine in a protein. This is the ingenious ' language that the cell uses to call specific amino acids to link up on peptides '. By now the triplet codes (*codons*) for all the twenty amino acids are known, so that if the base sequence of the DNA chain in a gene is known, reasonable predictions about the sequence of amino acids in the corresponding protein that is synthesised can be made. Conversely, from the amino acid sequence of a protein, the fine structure of the corresponding gene can be predicted.

A schematic picture of the process of protein synthesis in the living cell is given in Fig. 18.20. First, *m*-RNA with the base sequence complementary
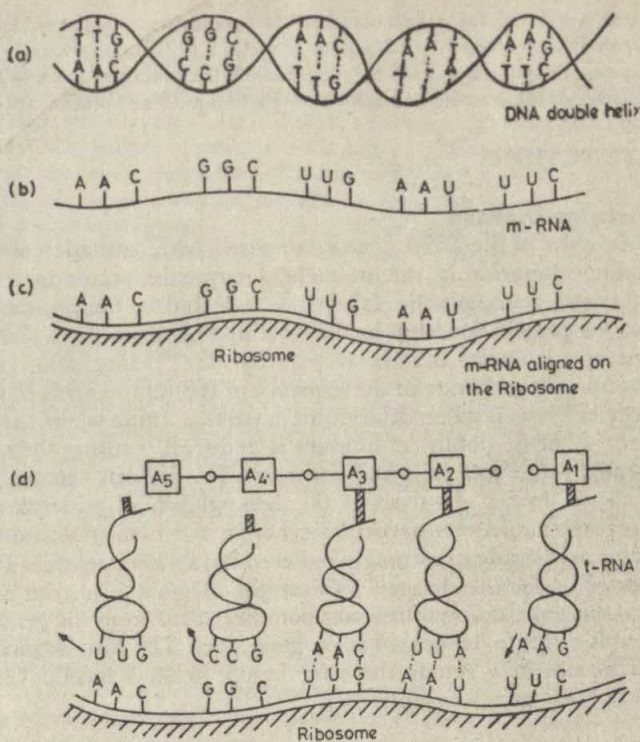
Fig. 18.20 Protein biosynthesis. (*a*) The coding molecule of DNA; (*b*) messenger RNA is first synthesised from the parent DNA, by complementary duplication; (*c*) the *m*-RNA aligns on ribosomal sites; (*d*) each transfer RNA with specific amino acid (denoted A, A_2...) pairs with the bases in *m*-RNA. Enzymatic synthesis of protein from the amino acids is activated here.

to that of the gene DNA is synthesised in the nucleus. Then it comes to the ribosome, where it attaches itself to the *r*-RNA of the ribosomes causing them to aggregate into the active polysome. In the meantime, specific *t*-RNA molecules complex with their appropriate 'activated' amino acids and travel to the polysome. A particular region in each *t*-RNA contains a reactive three-base sequence as shown in Fig. 18.20. Base pairing between the triplet codons in the *m*-RNA and the reactive triplet base sequence of the appropriate *t*-RNA occurs now.

If the reactive base triplet in phenylalanine-transfer-RNA were *AAA*, this *t*-RNA can base pair only with that region in the *m*-RNA that has a *UUU* sequence, and nowhere else. This is where the base pairing specificity is utilised to advantage in arranging the proper amino acid at the proper place for peptide bond formation. For example assume the base sequence in the *m*-RNA were to be as *UUU-AUC-AAA*...and so on. The *t*-RNA that has the reactive triplet *AAA* in it will bind to the *UUU* region of the *m*-RNA. No other *t*-RNA will bind here, because of the base pairing specificity. This *t*-RNA will carry with it the activated amino acid phenylalanine. The next code in *m*-RNA is *AUC*, the code for ileu. In this region of the *m*-RNA, only a *t*-RNA that carries the triplet *UAG* will bind. This *t*-RNA is specific for ileu. Likewise, lysine *t*-RNA will bind at the *AAA* site of *m*-RNA. In this way, a specific alignment of the *t*-RNA and hence of

of the amino acids is achieved. Once the amino acids of proper sequence (as dictated by the genetic code) are linked together successively via peptide bonds in a peptidation reaction catalysed by synthetase enzymes. Thus in a neat, assembly line fashion, the process of DNA → RNA transcription and RNA→protein translation is achieved in the living cell and proteins are synthesised.

18.7 MALFUNCTIONS

18.7.1 Molecular Disease

If the base sequence of the DNA gene is tampered with (mutation of the gene), a corresponding alteration in the amino acid sequence occurs in the protein that is synthesised. Such genetic defects are reflected in the protein structure and thus, in the protein function in the system. For example, a defect at one single point in the gene that is responsible for hemoglobin production causes a corresponding change in the sequence of the amino acids in the hemoglobin molecule. There is a hereditary trait in parts of India where the oxygenation efficiency of hemoglobin in humans is reduced, causing them to suffer from malformed red-blood cells and aenemia. This inborn hereditary disease is called *sickle cell anemia*. Analysis of the hemoglobin of patients with such conditions reveals that in one particular place in the hemoglobin molecule, a single glutamic acid residue is wrongly replaced by a valine residue. This single error is responsible for the disease, an example of what is termed a *molecular disease*. Since the protein is synthesised upon directions from the gene, the real error or ' mutation ' is to be located at the gene level. The cure for such a condition is then to somehow repair the error in the gene, a formidable and yet unachieved task of ' genetic engineering '.

18.7.2 How Does a Cell Age and Die?

In our discussion of the processes that go on inside a cell, we have been comparing the cell to a chemical factory. This implies that if the physical and environmental variables were kept constant, the efficiency of the cell to convert the input energy to output would be constant and unvaried as a function of time. Yet, we know that cells and tissues wear away and die with age. One obvious cause of ageing and death is malnutrition, (i.e. loss or deficiency of important chemicals in the input food). Besides this some other causes that lead to loss of cellular functions are: (*i*) errors or mutations at the gene level which get reflected at the functional level, (*ii*) modification of the enzymes and regulators that control biochemical reactions in the cell, and (*iii*) alteration of the structure and functions of the membranes in the cell. It appears likely that the process of ageing and death might arise not from any single cause, but by many that operate together. One notices that the connective tissues *collagen*, *elastin* and *retulin* are changed and toughened as a function of the age of the cell. These proteins are responsible for the flexibility and elasticity of tissues. With ageing of the system, one notices a loss of these properties, and also the formation of many crosslinks between individual collagen fibres. Some of the other effects seen upon ageing are: damage to cell membranes, peroxidation of lipids, and accumulation of certain dark pigments in cells.

One possible cause of all these effects has been suggested to be the formation and reactions of *free radicals*. Because of the presence of an unpaired electron, free radicals show high reactivities and readily combine with many compounds. A well-known reaction of free radicals is the abstraction of hydrogen atoms

from substrate molecules forming stable products. But in this abstraction process, the substrate molecule is rendered unstable and reactive.

Free radicals occur in nature and particularly in the cell as products of oxidation-reduction reactions, of radiation attack or chemicals in the cell, and by the action of heat and so on. In fact, it is suspected that broiling of meat or frying of many eatables produces free radicals. Chemicals that produce cancer such as the highly conjugated hydrocarbons are also sources of free radicals. With such easy access of free radicals, it is reasonable to expect that the radical would affect the chemicals inside the cell. Normally the cell possesses sufficient defence and preventive mechanisms against such attack but when reactions do occur, chemical modifications are induced.

The base thymine (T) that occurs in DNA is attacked easily and with such an attack, dimerises to produce T_2 (thymine dimer). Now, if in a gene, the T along the DNA sequence were chemically modified, it loses its base pairing ability with the result it loses its functionality as part of the genetic code. Such a radical induced alteration of T would then cause a 'misreading' or 'error reading' of the code. The m-RNA synthesised and the corresponding protein that is produced will now be of the ' wrong ' kind. At the functional level, this would amount to an error in the protein function or loss of efficiency. And if the modification or error in the T code is not repaired, duplicated DNA would also be altered. This is the so called ' point mutation ' that leads to genetic error leading to a loss of efficiency or to undesirable pathways in the cell.

Proteins are also subject to radiation effects and to attack by free radicals. The primary effect of radiation is to produce free radical centres in proteins, as also when attacked by free radicals from outside. Sulphur radicals from the cysteine moiety and ·CH radicals from saturated centres in the protein chains are the two most commonly occurring radicals in proteins. Radicals so formed may form covalent crosslinks between regions of one protein molecule, or beween two protein chains. This kind of radical induced chemical alteration of proteins leads to a loss of flexibility in connective tissue proteins, and to deactivation of enzymatic catalysis. When such effects accumulate over a period of time, the cellular machinery wears out and stops functioning.

Lipids, which form a minor source of food to the cell, and which also form part of the co-enzymes and membranes, are easily oxidised to yield peroxide radicals. Such a peroxidation leads to autoxidation of the lipids producing unwanted products, such as pigments. Radical transfer from lipid systems to the neighbouring enzymes deactivates catalytic processes. It is through such an autoxidation mechanism that the efficiency of the blood-clotting agents is reduced. Such effects lead to a loss of the viability of the cell work and burst the cell, a process called *hemolysis*. Thus it appears that at least one of the causes of ageing of the cell is brought about by chemical modification of the constituents.

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PROBLEMS

18.1 Can you think of the reason why DNA would be a double helix, but in general RNA is a single strand polymer?

18.2 What will happen to a solution of DNA in water when heated to about 100°C? What do you think will happen when this hot solution is cooled slowly and when cooled very rapidly?

18.3 From the data given in Table 18.1 and the value of the Avogadro number, estimate the weight of one cell of E. coli.

18.4 What are the forces that govern the conformation of a protein?

18.5 What do you expect the conformation of a protein to be in the extremes of pH (1 and 12)?

18.6 What is usually the time required for an enzyme catalysed reaction?

18.7 Why is a denatured enzyme inactive?

18.8 A protein, called trypsin inhibitor, can be denatured at 50°C. The increase in ΔH upon denaturation is $+57\cdot3$ kcal mol^{-1} which suggests the reaction is enthalpy-wise unfavourable. Yet ΔG at 50°C for the process is negative. What is the driving force for denaturation? Explain.

18.9 The peptide formation reaction:

$$ala(aq)+gly(aq) \rightarrow \text{Ala-gly}(aq)+H_2O$$
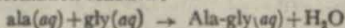
has a $\Delta G°$ value of 4130 cal mol^{-1} at standard conditions. Will the reaction go to completion if $C_{ala}=C_{gly}=0\cdot1\ m$ and $C_{ala\text{-}gly}=10^{-4}m$?

18.10 The equilibrium constants for the formation of Zn^{2+} complexes of glycine and cysteine are 5·5 and 9·9 respectively. Can you give a reason for this difference?

18.11 The amino acid glycine has the following equilibria in water solution:

$$^+NH_3-CH_2-COO^-$$
$$k_a \updownarrow \qquad (B) \qquad \updownarrow k_c$$
$$^+NH_3-CH_2-COOH \qquad NH_2-CH_2-COO^-$$
$$k_b \updownarrow \qquad\qquad \updownarrow k_d$$
$$NH_2-CH_2-COOH$$
$$(A)$$
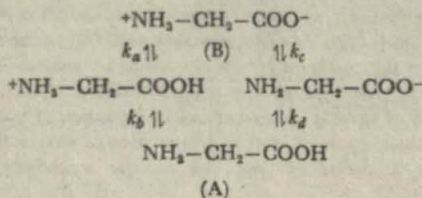
The value of k_a is of the order of 10^{-3}, $k_b \simeq 10^{-3}$. From this, can you say whether glycine will normally exists as the unionised form A or the doubly ionised from B in water?

19
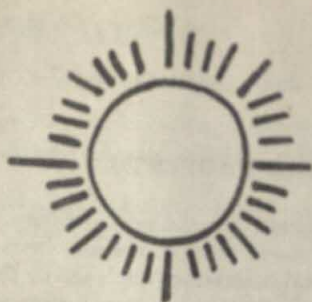
Nuclear Chemistry

People were transfixed with fright at the power of the explosion. Oppenheimer was clinging to one of the uprights in the control room. A passage from the Bhagvad Gita, ... flashed into his mind:

> *If the radiance of a thousand suns were to burst into the sky, that would be like the splendour of the Mighty One—*

yet, when the sinister and gigantic clouds rose up . . . . , he was reminded of another line from the same source:

> *I am become Death, the shatterer of world . . .*

ROBERT JUNGK
in *Brighter Than a Thousand Suns* while describing the first testing of the atom bomb

In Chapters 3 and 4 we have occasionally referred to those nuclear properties which are relevant to understand atomic and molecular behaviour. These include nuclear size, nuclear charge (i.e. atomic number), isotopes (section 3.2); nuclear transformations like radioactivity (section 3.1) and nuclear magnetism (section 4.10). Generally speaking, nuclear structure is of minor importance in chemistry, since nuclei remain intact in a vast majority of chemical reactions. However, a few nuclei under ordinary conditions, and all nuclei under special conditions, undergo changes leading to what are known as *nuclear reactions*. Examples of nuclear reactions are *radioactive decay, artificial transmutation, nuclear fission, and nuclear fusion*. Such reactions have either direct or indirect relevance to chemists. For instance, the phenomenon of radioactivity, apart from providing initial clues to atomic structure, has contributed to the widespread use of radioactive tracers for the solution of different types of chemical problems, and artificial transmutation has enabled chemists to synthesise the transuranic elements. The importance of nuclear fission and fusion need hardly be emphasised. While they threaten the very existence of human civilisation through weapons like atom bomb and hydrogen bomb, they also promise mankind an almost inexhaustible source of energy and prosperity through devices like nuclear reactors. Nuclear fusion is also responsible for solar energy—the primary energy source for life. We shall briefly discuss

all these topics in this chapter, pointing out their connection to nuclear structure wherever possible.

19.1 NUCLEAR STRUCTURE AND NUCLEAR PROPERTIES

Neutrons and protons, jointly referred to as *nucleons*, are the primary consti- tuents of all nuclei. The *atomic number* of a nucleus is equal to the number of protons while the *mass number* is equal to the total number of nucleons in the nucleus. In addition, several other elementary particles like *mesons* and *neutrinos* seem to be associated with nuclear structure in a manner which is not yet fully understood.

We have already seen that atoms and molecules are stable because the cou- lomb attraction between oppositely charged particles outweigh the coulomb repulsion between similarly charged particles. It is obvious that the coulomb interaction cannot account for the stability of nuclei, since they consist of only positively charged protons and chargeless neutrons. The origin of nuclear stability lies in the fact that nucleons attract each other by a force which is fundamentally different from either gravitational or electrostatic force and at the same time is much stronger. This new force, known as *strong interaction*, is charge independent (i.e. it exists between two protons, two neutrons or a proton and a neutron) and it operates only over a short distance (range) of about 10^{-13} cm. Because of its extreme short range, strong interaction is not significantly felt on a macroscopic scale; both gravitational and electrostatic interaction are long range and therefore exist on the micro- as well as macro- scale.

Nuclear structure is not as well understood as the electronic structure of atoms and molecules. Consequently, several alternative models have been proposed for the structure of nuclei. One such model, called the *nuclear shell model* bears considerable resemblance to the model of the atom and explains many nuclear properties. In this model, each nucleon is assigned four quantum numbers, one of which refers to the nucleon spin in a manner analogous to the spin quantum number of an electron. Every nucleus has a characteristic energy level pattern and the allotment of nucleons to the various energy states is regulated (similar to electron allotment in atoms and molecules), by the Pauli exclusion principle and the minimum energy principle. The pattern of nuclear energy levels is such that nuclei containing 2, 8, 20, 28, 50, 82 and 126 nucleons* of *each kind* have closed shell configurations. Such nuclei correspond to the inert configurations in atoms and, likewise, enjoy extra stability. Let us now survey some of the important nuclear properties like size, mass, binding energy, and magnetic behaviour.

Nuclear size: The approximate size of the nucleus was found to be of the order of 10^{-12} cm by Rutherford from a-particle scattering experiments (section 3.2). More accurate estimates can be obtained by studying neutron scattering since a neutron, unlike a-particles, can approach nuclei much closer due to the absence of coulomb repulsion. The sizes of various nuclei obtained this way are observed to obey the relation

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* These numbers are commonly called 'magic numbers' by nuclear scientists. Their explanation is one of the creditable achievements of the shell model.

$$r = r_0 \, A^{1/3}$$

where r is the radius, A the mass number of a given nucleus and r_0 a constant whose value is about $1\cdot3 \times 10^{-13}$ cm.

Example 19.1 Calculate the radius and the nuclear density of the nucleus of calcium of mass number 40. (Assume a spherical shape for the calcium nucleus.)

$$r = (1\cdot3 \times 10^{-13}) \, A^{1/3} \text{ cm}$$
$$= 1\cdot3 \times 10^{-13} \times (40)^{1/3} \text{ cm} = 4\cdot45 \times 10^{-13} \text{ cm}$$

Volume of the sphere $= \frac{4}{3} \pi r^3 = 3\cdot69 \times 10^{-37} \text{ cm}^3$

Mass of the nucleus $= \dfrac{A}{6.02 \times 10^{23}} \text{ g}$

Density of the nucleus $= \dfrac{\text{Mass}}{\text{volume}} = \dfrac{40}{6\cdot02 \times 10^{23}} \times \dfrac{1}{3\cdot69 \times 10^{-37}} \text{ g cm}^{-3} = 1\cdot8 \times 10^{14} \text{ g cm}^{-3}$

The above relation can be interpreted in a simple way. Since $r \propto V^{1/3}$ where V is volume, it follows that $V \propto A$. In other words, as the nucleon number increases the volume of nuclei increases proportionately. This means that nucleons behave as if they are hard spheres in contact with each other inside a nucleus, even though neutrons and protons actually are deformable. This is reminiscent of the situations we have met earlier where we found that atoms and ions under certain conditions (e.g. in the kinetic model of gases, or in the calculation of atomic radii of diatomic molecules and ionic crystals) behave as if they were rigid spheres. The calculation in the above example also shows the density of the nucleus to be enormously high. Such large values, not seen in the macroscopic world, indicate the fantastic packing arrangement in nuclei and also give us an idea of the magnitude of the 'strong interaction' that holds the nucleons together.

Nuclear mass: The mass number of a nucleus is equal to the number of nucleons in it. Two or more nuclei having the same number of protons but different number of neutrons will have the same atomic number but different mass numbers. Such nuclei are called *isotopes* and are designated as

$$\frac{\text{mass no.}}{\text{atomic no.}} \text{(symbol of element)}$$

e.g. $^{3}_{2}\text{He}$, $^{4}_{2}\text{He}$; $^{12}_{6}\text{C}$; $^{14}_{6}\text{C}$; (see section 3.2).

Since the mass of a neutron and a proton are nearly 1 amu each (proton $= 1\cdot007825$ amu, neutron $= 1\cdot008665$ amu), the masses of isotopes have nearly integral values. The exact mass of a nucleus is, however, never equal to, but always slightly less than the sum of the exact masses of the constituent nucleons. The exact mass of $^{2}_{1}\text{H}$ (deuterium) is $2\cdot014102$ amu whereas the sum of the nucleon masses (1 proton + 1 neutron) is $2\cdot016490$ amu, that is, $^{2}_{1}\text{H}$ is lighter than its constituents by $0\cdot002388$ amu. This difference, called the *mass defect*, has a fixed value for each nucleus and it is related to the *binding energy* of the nucleus.

Binding energy: Just as a particular number of electrons and nuclei form a stable molecule a particular number of nucleons also yield a stable nucleus due to lowering of potential energy. Analogous to molecules, nuclear stability can be expressed by the *nuclear dissociation energy*, which is the energy needed to convert a given nucleus to its component nucleons. However, it is conventional to use the term *binding energy* to express nuclear stability; the binding energy being equal to the dissociation energy in magnitude but opposite in sign. Nuclear binding energies differ from their molecular counterparts in two respects. Firstly, they are about million times larger and secondly they are practically temperature independent. This large binding energy is the main reason for nuclei remaining unaffected in usual chemical reactions.

Einstein's famous equation $E = mc^2$ shows that mass is another form of energy. Therefore, when mass (m) disappears, an equivalent amount of energy (mc^2) must be liberated and vice versa. We can now appreciate the significance of the mass defect referred to above. When a nucleus is formed, the energy of the system is lowered, and energy evolved. This amount is furnished by the conversion of mass into energy and consequently, we can readily calculate nuclear binding energies from a knowledge of mass defects, using Einstein's formula.*

Example 19.2 Calculate the binding energy of a deuteron.

The mass defect in deuteron is $-0 \cdot 002388$ amu which is equal to $-0 \cdot 002388$ g mol^{-1}. The binding energy (E) is, therefore,

$$E = \frac{-(0 \cdot 002388)(3 \times 10^{10})^2}{4 \cdot 18 \times 10^{10}} = -5 \cdot 1 \times 10^7 \text{ kcal mol}^{-1}$$

(NOTE: Division by $4 \cdot 18 \times 10^{10}$ is done to express energy in kcal.)

This value is enormously large compared to the 'binding' energies of molecules which are usually of the order of 10^2 kcal mol^{-1}. We may thus see that under the conditions of ordinary chemical reactions nuclei remain unaffected.

Energy levels: Nuclei, like atoms and molecules, can exist in several energy levels. Typical spacings between nuclear levels correspond to photons in the γ-ray region of the electromagnetic spectrum. The technique, known as *γ-ray spectroscopy*, is an important tool for the investigation of nuclear structure. Since the molecular environment perturbs nuclear levels to a slight but significant degree and since these shifts can be experimentally measured, nuclear spectroscopy is also very useful for studies of molecular structure.

Magnetism: As stated in our discussion of the shell model, one of the four quantum numbers assigned to neutrons and protons is similar to the spin quantum number of electrons. The nucleon quantum number also has only two permitted values and is a measure of the nucleon spin and hence of its magnetic

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*A similar technique cannot be used to calculate molecular dissociation energy because the mass equivalent of typical molecular dissociation energies (about 100 kcal mol^{-1}) is too small to be measurable. Molecular mass is, therefore, indistinguishable from the sum of atomic mass and one does not use the term 'mass defect' in case of molecules even though strictly speaking, there is a decrease in mass when a molecule is formed.

moment. The latter is, however, about 2000 times smaller than the electron magnetic moment since nucleon is about 2000 times heavier than an electron. In the so-called *even-even nuclei* (i.e. nuclei containing even number of neutrons and even number of protons such as $_6^{12}C$, $_8^{16}O$), all the nucleon spins are paired (by the Pauli principle) and such nuclei do not possess a permanent magnetic moment. A nucleus is paramagnetic if it has one or more unpaired nucleons as is the case with $_1^1H$, $_1^2H$, and $_7^{14}N$. It should be noted that a proton can pair only with a proton and a neutron only with a neutron. In other words, a proton never pairs with a neutron. Hence both $_1^2H$ and $_7^{14}N$ are paramagnetic, each with two unpaired nucleons ($1\,p$ and $1\,n$). We have already seen how magnetic nuclei like $_1^1H$ are used as powerful molecular probes in the technique of nuclear magnetic resonance (section 4.10). Nuclear magnetism is also responsible for the phenomenon of *adiabatic demagnetisation* which is used for the production of very low temperatures.

Shape: Though nuclei with net spin of zero or $\frac{1}{2}$ are spherical, those with spin greater than $\frac{1}{2}$ are invariably non-spherical. Careful experiments show that most such nuclei are ellipsoids. The charge distribution here obviously cannot be spherical and hence cannot be represented by a point charge. Rather it is approximated by two dipoles placed back to back. Such an arrangement is called a *quadrupole* and such charge distributions are characterised by a quadrupole moment (analogous to a dipole moment). Nuclei possessing electric quadrupole moments can be aligned in an external (non-uniform) electric field, resulting in states with different energy. (The process is quite similar to alignment of magnetic moment by magnetic fields as in NMR). Transition between quadrupole energy levels can be studied and they yield valuable information about molecular structures. This technique is known as nuclear quadrupole resonance (NQR) spectroscopy.

19.2 NUCLEAR REACTIONS

Nuclear reactions are those in which the nuclear composition changes. Some typical reactions are given below.

19.2.1 Radioactivity

We have mentioned earlier that the phenomenon of *radioactivity* results from the decay of unstable nuclei. Radioactivity is characterised by the emission of any or all of the following types of radiations termed alpha rays, beta rays and gamma rays. It has now been established that the alpha rays comprise helium nuclei. Thus an α-particle is simply a $_2^4He$ nucleus that has lost both its electrons and thus carries two positive charges. A β-particle is simply an electron $_{-1}^0e$, and a γ-particle is a high energy photon. Radioactive nuclei are usually found amongst the heavier elements and most nuclei with atomic numbers greater than 83 are radioactive.

When the nucleus of an atom ejects an α-particle, its mass number is reduced by four units and the charge number by two units. Since an α-particle is the nucleus of a helium atom, emission of an α-particle from a nucleus changes both the mass and the atomic number of the parent nucleus. Thus, the parent nucleus changes during an α-decay to yield the nucleus of a different atom. For example, the loss of an α-particle from a nucleus of uranium, $^{238}_{92}U$ produces a thorium nucleus $^{234}_{90}Th$. This is represented as

$$^{238}_{92}U \rightarrow ^{234}_{90}Th + ^{4}_{2}He$$
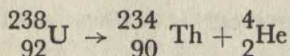
(As we would expect, a balanced equation for a nuclear reaction demands that the mass numbers and the charge numbers should separately balance.) An example of β-decay is the following reaction:

$$^{234}_{90}Th \rightarrow ^{234}_{91}Pa + ^{0}_{-1}e$$
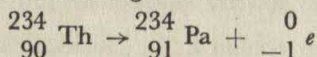
where $^{0}_{-1}e$ is the conventional symbol for indicating an electron (β-particle) in a nuclear reaction. Emission of a β-particle from a nucleus in effect increases the charge number (atomic number) by one, and results in the formation of a different nucleus. The emission of γ-ray on the other hand, does not bring about any change in either the mass number or the charge number of the nucleus since a γ-ray consists of only photons. Such γ-emissions take place from a nucleus in one of its excited states.

In addition to α-, β-, or γ-decay, a few nuclei decay by emitting positive electrons, or *positrons* $\left(^{0}_{+1}e\right)$, neutrons $\left(^{1}_{0}n\right)$, or protons $\left(^{1}_{1}H\right)$. Examples are:

$$^{22}_{11}Na \rightarrow ^{22}_{10}Ne + ^{0}_{+1}e$$

$$^{87}_{36}Kr \rightarrow ^{86}_{36}Kr + ^{1}_{0}n$$

$$^{43}_{21}Sc \rightarrow ^{42}_{20}Ca + ^{1}_{1}H$$
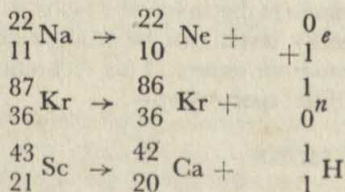
It is possible to understand in a simple manner the occurrence of radio-activity as well as the mode of decay by plotting the number of neutrons, N, against the number of protons, Z, for various nuclei (Fig. 19.1). It can be seen that the stable nuclei fall within a narrow belt indicated by the shaded region in the figure. The N/Z ratio for the lighter stable nuclei is close to unity while it increases to about 1·5 for heavier stable nuclei. This increase in the ratio for the heavier elements apparently means that as the number of protons increases, the number of neutrons increases even more to stabilise the nucleus by compensating for the greater coulomb repulsion. Nuclei lying outside the shaded region are unstable and they achieve stability by emitting such particles as would help in bringing their N/Z values close to that in the stability belt. For example, if a nucleus has a higher N/Z ratio (i.e. it lies to the left of the shaded region), then it can reduce this value either by decreasing N (emission of neutron) or increasing Z (emission of electron). Similarly, if a nucleus has a smaller

Fig. 19.1 The plot of number of neutrons (N) against number of protons (Z) for various nuclei. The stable nuclei fall within a narrow belt shown by the shaded region. Radioactive nuclei which fall on the left or the right of the stability belt decay in such a manner that their N/Z ratio approaches the ratio in the neighbouring stable nuclei.
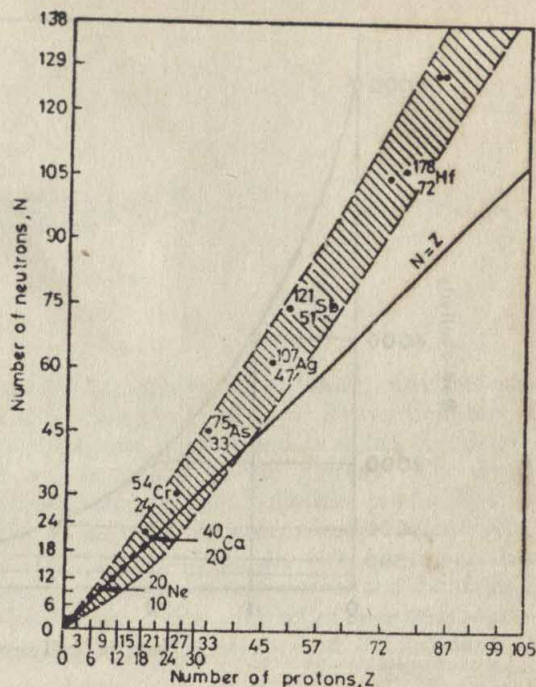
N/Z ratio (i.e. it lies to the right of the shaded region), then it can increase the ratio by emission of either α-particle, positron, or proton.

Rate of radioactive decay: The rate at which radioactive element decays is directly proportional to the amount of the element but it is independent of pressure and temperature. For example, for the reaction

$$A \rightarrow B + {}^{4}_{2}\text{He}$$
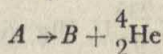
the rate of disappearance of $A = -\dfrac{d[A]}{dt} = \lambda[A]$

where $[A]$ is the number of atoms of A and λ, called the *decay constant*, is a characteristic constant for each radioactive element. This means that radioactive decay is similar to the chemical reactions obeying first order rate law (see section 13.2) and it, therefore, follows that $2\cdot303 \log \dfrac{[A]}{[A]_0} = -\lambda t$ where $[A]_0$ is the number of atoms of the radioactive element at the initial time, $t=0$. The time ($t_{1/2}$) called the *half-life* required for the number of atoms of A to become one-half of the initial amount is given by

$$-\lambda t_{1/2} = 2\cdot303 \log \dfrac{[A]_0}{2[A]_0}$$

$$\text{or } t_{1/2} = \dfrac{2\cdot303 \log 2}{\lambda} = \dfrac{0\cdot693}{\lambda}$$

Since λ is a constant for each radioactive element, the half-life, $t_{1/2}$, must also be a characteristic quantity for each element. The significance of half-life is that
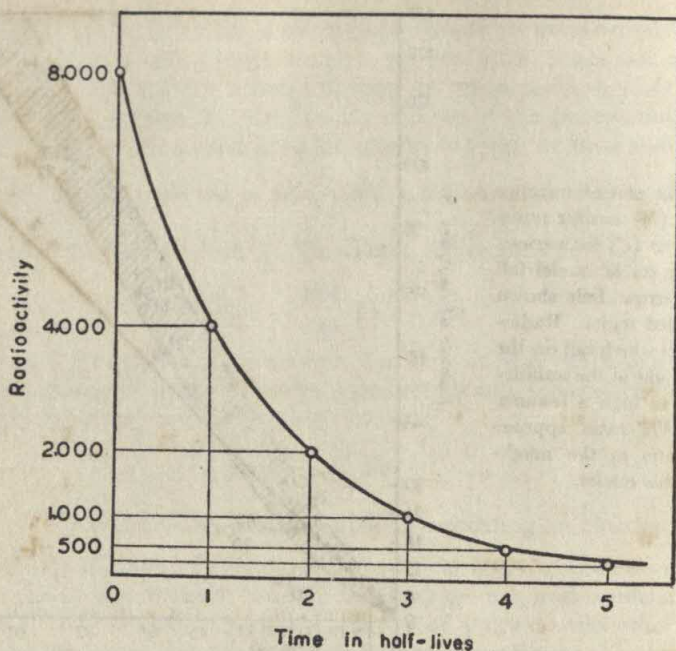
Fig. 19.2 A graph showing typical decay of radioactivity. The ordinate measures the time in unit of half-life while the abscissa gives a measure of the amount in arbitrary units.

it gives us an indication whether a particular decay is fast or slow. Its precise meaning can be illustrated by an example. $^{238}_{92}U$ has a half-life of $4·5 \times 10^9$ years. If we start with 100g of $^{235}_{92}U$, 50g will be left after $4·5 \times 10^9$ years, 25 g after $9·0 \times 10^9$ years, 12·5 g after $13·5 \times 10^9$ years and so on. Fig. 19.2 illustrates graphically a typical decay of radioactivity.

Example 19.3 A sample of radon emitted initially $7·0 \times 10^4$ α-particles per second; after some time, the emission rate became $2·1 \times 10^4$. What is the age of the sample? ($t_{1/2}$ for radon is 3·8 days)

From the equation of half-life one can deduce the relation
$$[A_t] = [A_0](0·5) t/t_{1/2}$$
Now the number of disintegrations per unit of time is directly proportional to the number of atoms present. Using the above equation

$$2·1 \times 10^4 = 7·0 \times 10^4 \ (0·5)^{t/3·8} \text{ days}$$
or $t = 6·6$ days

Therefore, the age of radon sample is 6·6 days.

Example 19.4 A sample of carbon from an ancient wooden frame gives 7·00 counts of $^{14}_{6}C$ per minute per gram of carbon. If freshly cut wood gives 15·3 counts of $^{14}_{6}C$ per minute, what is the age of the frame? ($t_{1/2}$ of $^{14}_{6}C$ = 5770 yr)

$$t_{1/2} = 0.693/\lambda$$

or $\lambda = 0.693/t_{1/2} = 0.693/5770$

$$\lambda = 1.20 \times 10^{-4} \text{ year}^{-1}$$

Now, $\log \dfrac{N_0}{N} = \dfrac{\lambda t}{2.303}$

or $\log \left(\dfrac{15.3 \text{ disintegration/min}}{7.00 \text{ disintegration/min}} \right) = \dfrac{(1.20 \times 10^{-4}) t}{2.30}$

or $t = \dfrac{2.303 \log 2.19}{1.20 \times 10^{-4}} = 6520 \text{ years}$

The frame is 6520 years old.

There are a number of heavy radioactive nuclei which, after undergoing spontaneous disintegration with the emission of α- or β-rays, yield the atom of a new element. The new element thus formed is called the 'daughter' while the radioactive reactant is named as the 'parent'. The daughter element may in turn be also unstable and emit radiations producing another new element. There may be a succession of such transformations with the creation of new elements at each step until finally a stable end-product is formed. All the elements thus formed, including the parent and the stable end-product, constitute a radioactive series. Three such series have been identified. These are: (1) uranium series, (2) thorium series, and (3) actinium series. One such series (uranium) is shown in Chart 19.1. Thus, $^{234}_{90}\text{Th}$ formed by the emission of α-particle from $^{238}_{92}\text{U}$ is the daughter element, $^{238}_{92}\text{U}$ being the parent element. Similarly $^{234}_{91}\text{Pa}$, $^{234}_{92}\text{U}$, $^{230}_{90}\text{Th}$, etc. are the daughter

Chart 19.1 Uranium Series

$^{238}_{92}\text{U} \xrightarrow[-\alpha]{4.5 \times 10^9 \text{y}} {}^{234}_{90}\text{Th} \xrightarrow[-\beta]{24.4 \text{d}} {}^{234}_{91}\text{Pa} \xrightarrow[-\beta]{1.14 \text{m}}$

$^{234}_{92}\text{U} \xrightarrow[-\alpha]{2.33 \times 10^4 \text{y}} {}^{230}_{90}\text{Th} \xrightarrow[-\alpha]{8.3 \times 10^4 \text{y}} {}^{226}_{88}\text{Ra} \xrightarrow[\alpha]{1540 \text{y}}$

$^{222}_{86}\text{Rn} \xrightarrow[-\alpha]{2.83 \text{d}} {}^{218}_{84}\text{Po} \xrightarrow[-\alpha]{3.05 \text{m}} {}^{214}_{82}\text{Pb} \xrightarrow[-\beta]{26.8 \text{m}} {}^{214}_{83}\text{Bi} \xrightarrow[-\beta]{19.7 \text{m}}$

$^{214}_{84}\text{Po} \xrightarrow[-\alpha]{1.5 \times 10^{-4} \text{s}} {}^{210}_{82}\text{Pb} \xrightarrow[-\beta]{22 \text{y}} {}^{210}_{83}\text{Bi} \xrightarrow[-\beta]{5 \text{d}}$

$^{210}_{84}\text{Po} \xrightarrow[-\alpha]{140 \text{d}} {}^{206}_{82}\text{Pb}$
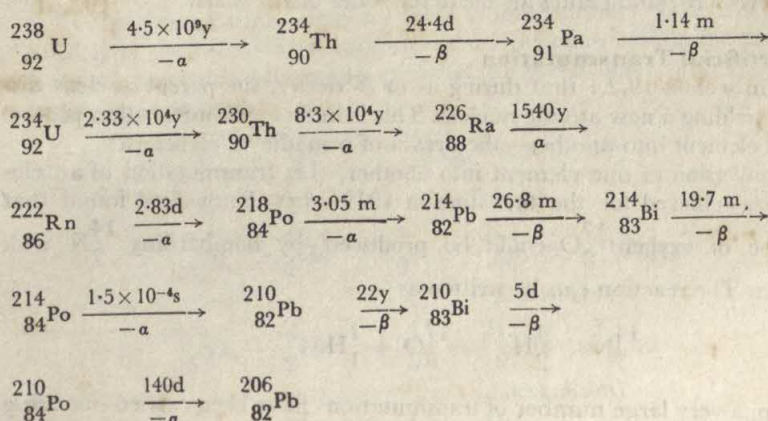
[1]The abbreviations y, d, m, and s stand for year, day, minute and second respectively.

elements produced, respectively, from the parent elements $^{234}_{90}$Th, $^{234}_{91}$Pa, $^{234}_{92}$U, etc. The value given above each arrow is the half-life of the parent element involved.

Determination of the age of a sample—an application of radioactivity:
A problem of great importance in archaeology, geology, lunar exploration, and many other fields is the determination of the age of a particular sample. It is possible to solve this problem if the sample contains some radioactive isotope, preferably one with very long half-life. Example 19.4 dealt with the determination of the age of a sample using its decay rate. Let us say that we wish to find the age of a rock which contains some $^{238}_{92}$U. From the moment of its formation $(t=0)$, the $^{238}_{92}$U present in it would disintegrate yielding the various members of the uranium series. The end product of this series is the non-radioactive element $^{206}_{82}$Pb. Since the half-life of uranium is much longer than that of any other intermediate member of the series, it is reasonable to assume that virtually the disintegrating $^{238}_{92}$U has been converted into $^{206}_{82}$Pb (an example of the slowest step being the rate-determining step; see Chapter 13). If one further assumes that the lead isotope was not initially present, then it is a simple matter to determine the age by measuring the concentration of $^{238}_{92}$U and $^{206}_{82}$Pb. For example, let the measured ratio Pb:U be unity. This means that half of the uranium isotope has been converted to the lead isotope. The age of the rock, therefore, must be equal to $t_{1/2}$ of $^{238}_{92}$U, i.e. the rock must be 4.5×10^9 years old.

Actually most rocks and minerals having uranium and lead give a $^{206}_{82}$Pb:$^{238}_{92}$U ratio of 1.33×10^{-2} indicating an age of the order of 10^8 years.

19.2.2 Artificial Transmutation
We saw in section 19.2.1 that during α- or β- decay, the parent nucleus disappears, yielding a new atomic nucleus. This is in fact a transmutation process from one element into another—the dream of a medieval alchemist!

The conversion of one element into another, (i.e. transmutation of an element), was achieved for the first time in 1919 when Rutherford found that an isotope of oxygen $^{17}_8$O could be produced by bombarding $^{14}_7$N with α-particles. The reaction can be written as

$$^{14}_7\text{N} + {}^4_2\text{He} \rightarrow {}^{17}_8\text{O} + {}^1_1\text{H}$$
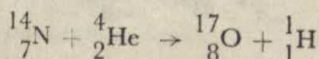
Since then, a very large number of transmutations have been carried out using α-particles, neutrons, protons, deuterons, and some heavier nuclei. It is hard to predict precisely what happens at the time of collision of the fast or slow moving particles with the stable nucleus. Generally, several different nuclear reactions

occur simultaneously after collision. Thus, $_{29}^{63}Cu$, upon bombardment by deuterons $\left(_{1}^{2}H\right)$, may lead to the following reactions:

$$_{29}^{63}Cu + _{1}^{2}H \rightarrow _{30}^{65}Zn$$

$$\nearrow _{30}^{64}Zn + _{0}^{1}n$$

$$\rightarrow _{30}^{63}Zn + 2_{0}^{1}n$$

$$\searrow _{29}^{64}Cu + _{1}^{1}H$$
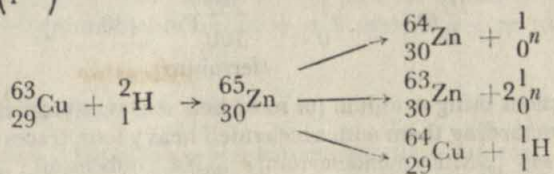
If charged particles like protons and α-particles are used for bombardment, there would be repulsion between the bombarding particles and the target nucleus due to their like charge. To overcome the repulsion, the particles must have considerable energy. In order to produce such energetic particles, scientists have constructed several types of accelerators in which energy is transferred to particles from electric and magnetic fields as in the van de Graaf particle accelerator, and other accelerators termed the cyclotron, the synchroton and the bevatron. It is possible now to accelerate a proton in such accelerating machines to velocities corresponding to kinetic energies of the order of billions of electron volts. On the other hand, neutrons are particularly effective in initiating nuclear reactions as they do not encounter any repulsive force from a nucleus. Its effectiveness can be judged by the fact that every known nucleus becomes unstable after absorbing a neutron.

By making use of the particle bombardment technique, elements like technetium, astatine, francium, promethium and the transuranic elements have been artificially synthesised. The first transuranic element, $_{93}^{239}Np$, was prepared in 1940 by bombarding $_{92}^{238}U$ with neutrons.

$$_{92}^{238}U + _{0}^{1}n \rightarrow _{92}^{239}U \rightarrow _{93}^{239}Np + _{-1}^{0}e$$
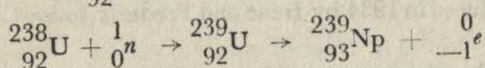
At the present time, elements from atomic number 92 to 104 have been artificially produced. The nuclear reaction schemes used in the production of some of these trans-plutonium elements are given below with their half-lives shown in parentheses:

$$_{94}^{240}Pu + _{1}^{1}H \rightarrow _{95}^{241}Am \quad (470 \text{ years})$$
$$\text{(americium)}$$

$$_{94}^{239}Pu + _{2}^{4}He \rightarrow _{0}^{1}n + _{96}^{242}Cm \quad (162 \text{ days})$$
$$\text{(currium)}$$

$$_{95}^{241}Am + _{2}^{4}He \rightarrow 2_{0}^{1}n + _{97}^{243}Bk \quad (4 \cdot 6 \text{ hours})$$
$$\text{(berkelium)}$$

$$_{92}^{238}U + _{6}^{12}C \rightarrow 4_{0}^{1}n + _{98}^{246}Cf \quad (35 \cdot 7 \text{ hours})$$
$$\text{(californium)}$$

$$\underset{92}{238}U + \underset{7}{14}N \rightarrow 5\underset{0}{1}n + \underset{99}{247}Es \quad (7\cdot3 \text{ min})$$

(einsteinium)

$$\underset{92}{238}U + \underset{8}{16}O \rightarrow 2\underset{0}{1}n + \underset{100}{252}Fm \quad (30 \text{ min})$$

(fermium)
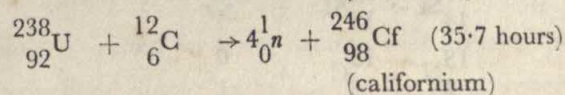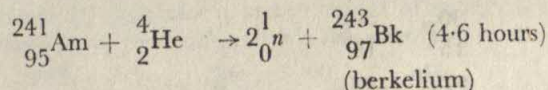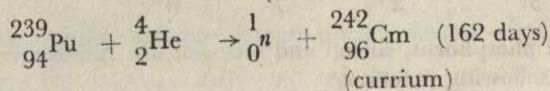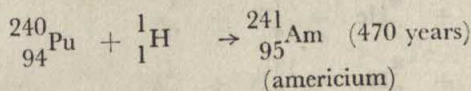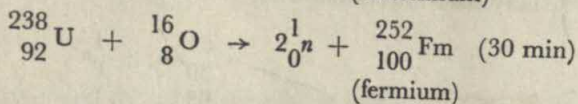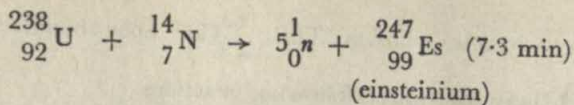
By similar reactions using uranium (or some heavier trans-uranium element) as targets and bombarding them with accelerated heavy ions, traces of elements of atomic numbers $_{101}$Md (mendelevium), $_{102}$Na (nobelium), $_{103}$Lw (lawrencium), and also 104 and 105 have been synthesised. All these high atomic number elements are unstable and decay by α-emission and/or by spontaneous fission.

Example 19.5 An isotope of element 105 was prepared by bombarding a $\underset{98}{249}$Cf target with $\underset{7}{15}$N nuclei. After absorbing $\underset{7}{15}$N, $\underset{98}{249}$Cf emits four neutrons. Write the equation for the nuclear reaction.

The reaction is

$$\underset{98}{249}Cf + \underset{7}{15}N \rightarrow \underset{105}{260}X + 4\underset{0}{1}n$$
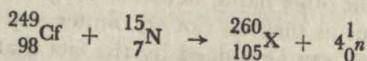
We will describe the chemistry of these elements in the latter part of this chapter.

Artificial radioactivity: The first man-made radioisotopes $\underset{15}{30}$P, $\underset{14}{27}$Si and $\underset{7}{13}$N, were produced in 1934 by Irene and Frederic Joliot-Curie by using $\underset{13}{27}$Al, $\underset{12}{24}$Mg and $\underset{5}{10}$B as the targets and bombarding them with α-particles.

$$\underset{13}{27}Al + \underset{2}{4}He \rightarrow \underset{15}{30}P + \underset{0}{1}n$$

$$\underset{12}{24}Mg + \underset{2}{4}He \rightarrow \underset{14}{27}Si + \underset{0}{1}n$$

$$\underset{5}{10}B + \underset{2}{4}He \rightarrow \underset{7}{13}N + \underset{0}{1}n$$
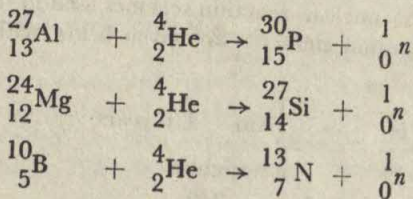
These isotopes of phosphorus, silicon and nitrogen are radioactive and decay according to the following reactions:

$$\underset{15}{30}P \rightarrow \underset{14}{30}Si + \underset{+1}{0}e$$

$$\underset{14}{27}Si \rightarrow \underset{13}{27}Al + \underset{+1}{0}e$$

$$\underset{7}{13}N \rightarrow \underset{6}{13}C + \underset{+1}{0}e$$
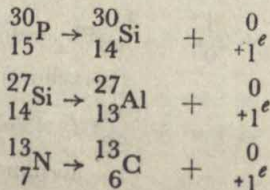
Radioactivity produced in this manner in common stable elements is called *artificial radioactivity* and this type of transmutation has enabled chemists to synthesise hundreds of radioisotopes not found in nature. Such artificially prepared radioisotpes have found a large number of uses in physico-chemical research, biology, medicine, industry and agriculture, as will be mentioned later.

19.2.3 Nuclear Fission

When uranium isotope-235 is bombarded with slow neutrons, $^{236}_{92}U$ is formed by capturing a neutron. The $^{236}_{92}U$ being unstable breaks up into two fragments besides releasing two or three neutrons.

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{236}_{92}U \rightarrow ^{140}_{56}Ba + ^{94}_{36}Kr + 2^{1}_{0}n$$
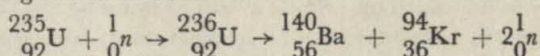
The above is a typical fission reaction. Several other isotopes of heavier elements (e.g. platinum, bismuth, etc.) undergo fission but only when bombarded with projectiles of very much higher energy. During nuclear fission a large amount of energy is released due to mass loss, i.e. the sum of the masses of the two fragments and the neutrons set free, is less than the sum of the masses of the reactants. This mass loss in uranium fission is of the order of 0·2 amu which corresponds to 186 million electron volt (MeV) per uranium atom fissioning or about $4·3 \times 10^9$ kcal per mole of uranium atoms fissioning. This represents a tremendous amount of release of energy.

The fission process is complicated by the fact that a given nucleus undergoing fission may split in a variety of alternative ways. Over thirty pairs are known. Following are some possible ways of fission of the uranium nucleus.

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{236}_{92}U$$

$$\rightarrow \,_{57}La + \,_{35}Br + 2^{1}_{0}n$$
$$\rightarrow \,_{56}Ba + \,_{36}Kr + 2^{1}_{0}n$$
$$\rightarrow \,_{55}Cs + \,_{37}Rb + 2^{1}_{0}n$$
$$\rightarrow \,_{54}Xe + \,_{38}Sr + 2^{1}_{0}n$$
$$\rightarrow \,_{52}Te + \,_{40}Zr + 2^{1}_{0}n$$
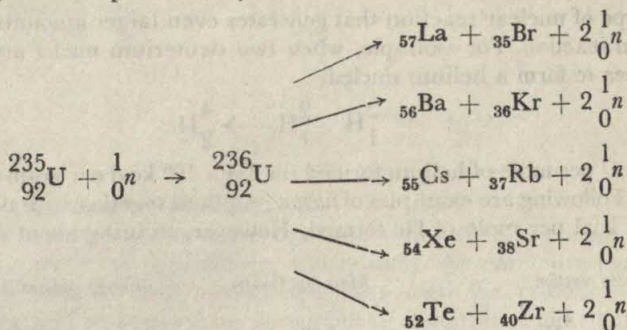
Let us now consider the most famous nuclear fission—that of $^{235}_{92}U$ brought about by neutron capture. Although this fission process occurs in a large number of ways, in each case a large amount of energy is released and more than one (secondary) neutron emitted. For example, in the mode,

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{236}_{92}U \rightarrow ^{90}_{37}Rb + ^{144}_{55}Cs + 2^{1}_{0}n$$
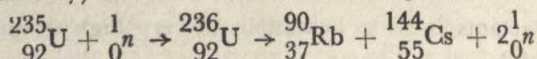
two neutrons are emitted for every neutron that initiates the fission process. The neutrons emitted during fission may be further absorbed by other $^{235}_{92}U$

nuclei thus causing further fission and emission of more neutrons. In this way a *chain reaction* starts releasing tremendous amount of energy. However, if the amount of ^{235}U is small, most of the neutrons will escape from the surface and the reaction will stop. Therefore, a *critical mass* of metallic uranium is necessary in order to start and sustain a chain reaction. The critical mass of $^{235}_{92}$U has been found to be between 1 to 100 kg.

The basic principle of an atomic bomb is the chain reaction. At the time of explosion two samples each of subcritical mass, but whose total mass exceeds the critical mass, are brought together by the use of ordinary explosives. Once these subcritical masses come together, a chain reaction starts releasing a large amount of energy. One gram of $^{235}_{92}$U evolves upon fission about 2×10^7 kcal of energy.

Nuclear reactions: The principle underlying such nuclear fission has also been employed in harnessing vast amounts of energy in nuclear reactors. In these reactors, the fission reaction is made to occur at a controlled rate. Essentially a reactor consists of lumps of $^{235}_{92}$U separated from each other by blocks of graphite or 'heavy water', D_2O, (neutron moderating materials) which, by slowing the neutrons, help in controlling the chain reaction. The large amount of energy in the form of heat which is released during the reaction is converted into electrical energy. Two such nuclear power plants have been set up at Tarapur and Kotah in India and some more are being planned.

19.2.4 Nuclear Fusion

Another type of nuclear reaction that generates even larger amounts of energy is the fusion reaction. For example, when two deuterium nuclei are made to fuse together to form a helium nucleus

$$^2_1H + {}^2_1H \longrightarrow {}^4_2He$$
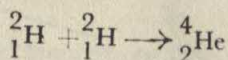
$5 \cdot 5 \times 10^8$ kcal per mole of helium formed (or $1 \cdot 4 \times 10^8$ kcal per gram of helium) is released. Following are examples of fusion reactions together with the energies released in kcal per mole of He formed. However, to bring about such fusion

Fusion reaction	Mass loss (amu)	Energy released (kcal/mol He)
$^2_1H + {}^2_1H \rightarrow {}^4_2He$	0·026	$5 \cdot 5 \times 10^8$
$^2_1H + {}^3_1H \rightarrow {}^4_2He + {}^1_0n$	0·012	$4 \cdot 1 \times 10^8$
$4^1_1H \rightarrow {}^4_2He + 2{}^0_1e$	0·029	$6 \cdot 2 \times 10^8$

reactions, the reactants have to be initially at very high temperatures of the order of 10^7–10^8 °C.

In the last twenty years or so, scientists have used fusion reactions to make the so-called hydrogen (thermonuclear) bomb. The technology of fusion bombs is different from that of fission bombs (atom bomb). In order to attain the

very high temperature required to initiate the fusion reaction of the type, $_1^2H + _1^2H \rightarrow _2^4He$, an atomic bomb is used as a trigger.

Of the fusion reactions listed above, the last one, namely

$$4_1^1H \rightarrow _2^4He + 2_1^0e$$
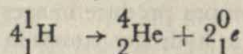
is of special importance. It is this reaction which is believed to be taking place in the Sun and in the stars. All the heat and light we get from the Sun is due to the energy released in this reaction resulting from the large mass loss. The Sun is believed to be a vast mass of hydrogen gas at a high temperature of the order several hundred million degrees. At this temperature the above thermo-nuclear reaction occurs with high efficiency. The net reaction consisting of the fusion of four hydrogen nuclei into a helium nucleus with the ejection of two positrons is supposed to be effected with the help of a catalyst of carbon and nitrogen nuclei which are consumed and reformed in each cycle as shown in Fig. 19.2. This energy cycle, referred to as the carbon-nitrogen solar energy cycle, was first suggested by Weiszacker and Bethe.

Fig. 19.3 The carbon–nitrogen solar energy cycle. The net reaction is

$$4_1^1H \rightarrow _2^4He + 2_1^0e + \text{energy}$$
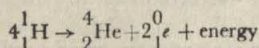
The energy release in various steps is indicated by γ.
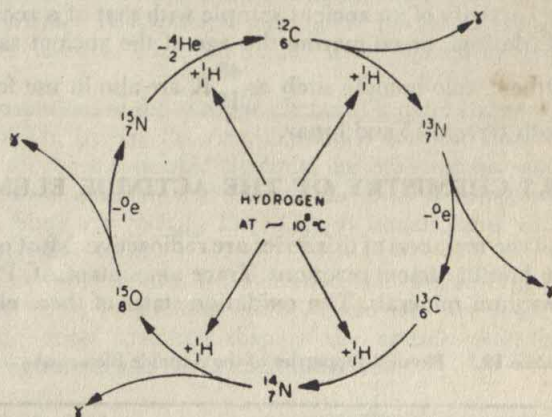
19.2.5 Applications of Radioactivity

The use of radioisotopes as *tracers* has been widespread in chemistry, biology engineering, medicine, agriculture, and industry. An early investigation of the diffusion of ions in solid metals and salts used the radioisotope of lead. Radioactive lead was coated on the surface of a sample of metallic lead. After regular intervals, thin slices were cut and the radioactivity measured. From the observed distribution of the tracer into the solid at different times, the kinetics of diffusion could be determined, thus helping to understand the nature of the solid state.

The application of the tracer techniques in elucidating reaction mechanisms was discussed in Chapter 13.

Radioactive isotopes are used extensively in biochemistry and molecular biology. A common use is in the determination of the pathway of biologically interesting compounds in the cell. For example, an amino acid in which ^{12}C has been replaced by radioactive ^{14}C is introduced into a cell culture, and in the biosynthetic reactions, labelled carbon atoms are incorporated into proteins.

The amount incorporated in various fractions leaving a separating column can be measured using a radioactivity counter. Autoradiography is another tool that is based on the distribution of radioactive atoms, and this has been of great use in modern biology. It uses the fact that electrons and photons emitted by the decay of radioisotopes produce images on special photographic emulsion. For example, certain hydrogen atoms in the base thymine (T) in DNA molecules (see Chapter 18) can be easily replaced by radioactive tritium $\left(^{3}_{1}\text{H}\right)$ If this labelled DNA molecule (or a chromosome containing this labelled DNA) were placed on a slide coated with photographic emulsion, the tritium atoms can be 'seen' on the slide. The shape, location and mobility of the DNA molecules in cells can be thus monitored by autoradiography.

γ-rays emitted by radio cobalt $\left(^{60}_{27}\text{Co}\right)$ and other metals are used in surgery to burn unwanted tissues such as cancer growths. Such an application of radioactivity in medicine is termed as radiotherapy or radiosurgery.

The use of radioactive isotopes in geology depends on the kinetics of radioactive decay. ^{14}C decays with a half-life of about 5700 years. Comparison of ^{14}C activity of an ancient sample with that of a recent sample affords a means of 'dating', or estimating the age of the ancient sample (see Example 19.4). Other radio-isotopes such as $^{40}_{19}\text{K}$ are also in use for such studies on samples, both terrestrial and lunar.

19.3 CHEMISTRY OF THE ACTINIDE ELEMENTS

All the members of this series are radioactive. Most of the elements are produced by bombardment reactions. Trace amounts of At, Pa, Np and Pu are found in uranium minerals. The oxidation states of these elements are given in Table

Table 19.1 Physical Properties of the Actinide Elements[1]

Element	Symbol	Oxidation states[2]	Ionic radius, A M^{3+}	M^{4+}	melting point °C	density g/co	atomic volume A^3
Actinium	Ac	3	1·11	0·99	1100	–	–
Thorium	Th	3, 4̄	–	0·96	1750	11·7	19·8
Protactinium	Pa	3, 4̄, 5	–	0·93	1600	13·4	14·7
Uranium	U	3, 4, 5̄, 6	1·03	0·93	1132	19·0	12·6
Neptunium	Np	3, 4̱, 5̱, 6	1·01	0·92	637	20·5	11·6
Plutonium	Pu	3̱, 4̱, 5̱, 6	1·00	0·90	639	19·7	12·1
Americium	Am	3̱, 4̱, 5̱, 6	0·99	0·89	995	13·7	18·0
Curium	Cm	3̱, 4	0·99	0·88	1340	–	–
Berkelium	Bk	3̱, 4	0·98	–	–	–	–
Californium	Cf	3	0·98	–	–	–	–

[1]Experimental data for the elements einsteinium, fermium, mendelevium, nobelium, lawrencium and hahnium are not yet available.

[2]States which are underlined are the most common states.

19.1 and the most stable oxidation state is underlined in each case. In the cases of uranium and other actinide elements, the higher oxidation states of the metal occur in compounds such as the oxy-cations rather than as the free metal ions, e.g. UO^+_2, UO_2^{2+}, and so on.

Ac^{3+} and Th^{4+} are colourless. The $+3$ actinide ions have a greater tendency to hydrolyse and to form complexes than the $+3$ lanthanide ions. The order of the complexing tendency in the actinide series is $M^{4+} > MO^+_2 > M^{3+} > MO_2.^+$ The order of affinity amongst different mononegative anions of most of the actinide ions is $F^- > NO_3^- > Cl^- > ClO_4^-$ and amongst the dinegative anions, the order is $CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$. The solubility of various actinide compounds in $+3$ oxidation state is similar to that of the lanthanide compounds in their $+3$ oxidation state. M^{4+} ions can be precipitated as iodates, and MO^+_2 ions as carbonates. The separation of the ions of the series following americium is done by ion-exchange methods, similar to the ones used for the lanthanons. Thus the elements from Am to Lw are eluted by citrate buffer in a separation column. The order of elution is related inversely to the atomic number.

The actinide metals are attacked by oxygen at temperatures above 250°C and by nitrogen above 800°C. They are also attacked by hot water. Reaction with acids is slow and concentrated HNO_3 makes the metals passive. They all react with halogens to give halides. Uranium reacts with sulphur to give uranium sulphide.

Isomorphism amongst compounds of the actinide elements is quite common. Thus, the dioxides (MO_2) of Th, U, Np, Pu, Am, crystallise with the fluorite structure. The trihalides of all the transuranic elements are isomorphous with those of lanthanides. Thorium, uranium and plutonium form isomorphous series KMF_5 and KM_2F_9. Similarly $(NH_4)_2$ $Th(NO_3)_6$ is isomorphous with $(NH_4)_2$ $Pu(NO_3)_6$ and $(NH_4)_2$ $Ce(NO_3)_6$.

The electronic spectra of actinide ions in $+3$ oxidation state are similar to that of lanthanide elements in $+3$ oxidation state. These ions are highly paramagnetic. The actinide series members display the *actinide contraction* which is similar to the contraction seen in the lanthanide series.

SUGGESTED READING

G. R. CHOPPIN, *Nuclear and Radiochemistry*, Benjamin, Inc., New York (1964).

B. G. HARVEY, *Introduction to Nuclear Chemistry and Physics*, Prentice Hall, Englewood Cliffs, New Jersey (1962).

T. R. OVERMAN, *Basic Concepts of Nuclear Chemistry*, Reinhold Publishing Corporation, New York (1963).

PROBLEMS

19.1 Calculate the absolute charge carried by the nucleus of a carbon atom.

19.2 Complete the following equations:

(a) $^{238}_{92}U \rightarrow {}^{234}_{90}Th + \text{\_\_\_\_}$

(d) $^{234}_{90}Th \rightarrow {}^{0}_{-1}e + \text{\_\_\_\_}$

(b) $\text{____} \rightarrow {}^{234}_{92}U + {}^{0}_{-1}e + $

(e) $^{234}_{92}U \rightarrow {}^{230}_{90}Th + \text{\_\_\_\_}$

(c) $^{230}_{90}Th \rightarrow \text{\_\_\_\_} + {}^{4}_{2}He$

(f) $\text{\_\_\_\_} \rightarrow {}^{222}Rn + {}^{4}_{2}He$
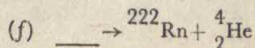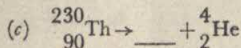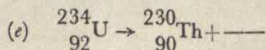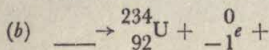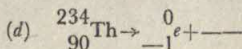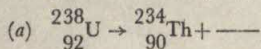
19.3 The isotope $^{60}_{27}$Co has a half-life of 5·27 yr. What amount of a 0·1000 g sample of $^{60}_{27}$Co will remain after one year?

19.4 A radioisotope decays in such a manner that after one hour, only 25 per cent of the initial amount remains. Calculate the decay constant and half-life of the isotope.

19.5 A sample of carbon from an ancient tree is found to give 4·00 counts per minute per gram of carbon due to its $^{14}_{6}$C content. What is the approximate age of the tree? (Half-life of $^{14}_{6}$C = 5770 years and a freshly cut wood gives 15·3 counts per minute.)

19.6 (a) What is the mass loss in amu when a helium nucleus is formed from two protons and two neutrons? (Masses of hydrogen, neutron and helium are 1·0078, 1·0087 and 4·0026 amu respectively.)

(b) What is the binding energy of helium?

19.7 Calculate the ΔE for the reaction: $^{7}_{3}$Li + $^{1}_{1}$H → $2 ^{4}_{2}$He. Atomic masses: ^{7}Li = 7·016, $^{1}_{1}$H = 1·008, ^{4}He = 4·003 amu.

19.8 Which of the following nuclei should have zero magnetic moment?

$$^{1}_{1}H; \quad ^{6}_{3}Li; \quad ^{8}_{4}B; \quad ^{12}_{6}C; \quad ^{13}_{6}C; \quad ^{16}_{8}O; \quad ^{17}_{8}O; \quad ^{32}_{16}S$$
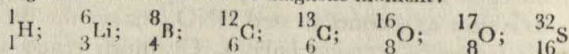
Molecular Models

Three-dimensional models are helpful aids in the visualisation of molecules in space. There are several types of molecular models and a student should be familiar with at least some of these.

The simplest of molecular models is the ball-and-stick type. In this set, the carbon atoms are represented by wooden spheres (painted black) and the bonds by wooden pegs of different lengths denoting single, double and triple bonds; wooden spheres with different colours are used for other atoms. These models are useful in showing the geometric relationships, but are not accurate as to interatomic distances.

There is another type of model in which the sizes of the atoms are not shown but interatomic distances are accurately represented. 'Barton models' and 'Drieding models' come under this category. In 'Drieding models' the atoms and bonds are constructed of four metal rods joined together at the center of the carbon atom at the correct tetrahedral angle of 109° 28'. Interatomic distances can be accurately measured (scale, 1 A=2·5 cm) using these models and they are very helpful in the study of stereochemistry. In Barton models (scale, 1 A=10 cm), carbon atoms are represented by metal tetrahedra, triangular prisms and so on, depending on the type of hybridisation; the bonds are represented by metal rods. They are excellent for demonstration purposes in larger classes.

In another type of model, both interatomic distances and atomic sizes are accurately shown. 'Fisher-Hirschfelder-Taylor models' (scale, 1 A=1 cm) and 'Stuart-Briegleb models' (scale, 1 A=1·5 cm) are of this type.

There is yet another type of models which permits one to visualise the molecular orbital structure, in addition to the position of atoms in molecules. This is the 'Framework Molecular Orbital Models' supplied by the Prentice-Hall, Inc. (USA). Students are encouraged to be familiar with the different types of molecular models.

Ball and stick models of methane (left), cyclopentane (middle), and ethylene (right)
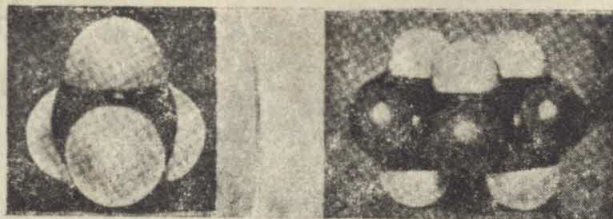
Stuart - Briegleb models of methane (left) and cyclohexane (right)
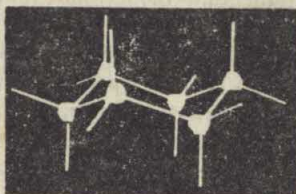
Barton model of cyclohexane
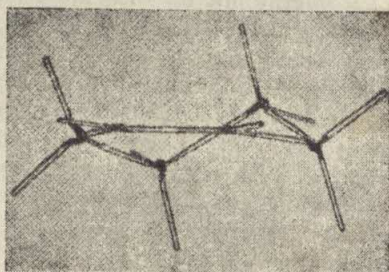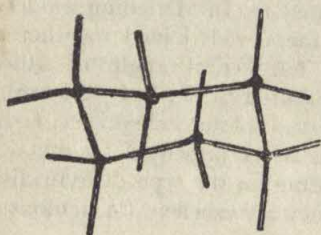
Drieding models of cyclohexane (left) and cyclohexene (right)

SI Units

Conventionally, two systems of units have been mainly in use in expressing physical quantities: the centimetre-gram-second (CGS) system, and the foot-pound-second (FPS) units system. Adoption of more than a single system has given rise to confusion in scientific literature. Besides, there have been as many as three units of measuring temperature. By international agreement, there has been a world-wide change over to a common universal system of units, termed the SI (Systemé Internationale) Units. The following tables summarise the different SI units and their symbols.

Table B. 1. Names and Symbols of some SI Units

Physical quantity	Symbol for physical quantity	SI Unit	Symbol for SI Unit	Remarks
Primary Units				
Length	l	metre	m	
Mass	m	kilogram	kg	
Time	t	second	s	
Electric current	I	ampere	A	
Thermodynamic temperature	T	kelvin	K	The symbol (°) and the word degree should not be used with kelvin.
Luminous intensity	I_v	candela	cd	
Quantity of substance	n	mole	mol	Not yet officially adopted
Secondary Units				
Plane angle		radian	rad	
Solid angle		steradian	sr	

Table B. 2 Derived SI Units with Special Names

Physical quantity	Symbol for physical quantity	SI Unit	Symbol for SI Unit	Relation to other SI Units
Force	F	newton	N	$kg\ m\ s^{-2}$
Energy	E, W	joule	J	N m
Power	P	watt	W	$J\ s^{-1}$
Electric charge	Q	coulomb	C	A s
Electric potential	V	volt	V	$J\ Q^{-1}$
Electric resistance	R	ohm	Ω	$V\ A^{-1}$
Frequency	f	hertz	Hz	s^{-1}
Temperature	t	degree Celsius	°C	t °C

Table B. 3   SI Units for Use in Special Fields

Quantity	SI Unit	Symbol for the unit	Value
Energy	electron volt	eV	$1·602\ 1 \times 10^{-19}$ J
Mass of an atom	atomic mass unit	amu	$1·660\ 4 \times 10^{-27}$ kg
Length	astronomic unit	(A.U)	$1·496\ \times 10^{8}$ km
Length	Parsec	parsec	$3·093\ \times 10^{13}$ km

Dimensional Analysis

Length (l), mass (m) and time (t) are the three fundamental quantities used to express other physical quantities. Standards for their measurements are chosen and fixed by convention, and units of their measurements are chosen by convenience with reference to the standards. In chemistry and physics, we use certain common units for many quantities, all of which are reducible to the fundamental dimensions of l, m and t as illustrated below.

Quantity	Conventional unit	Dimension
Velocity (distance/time)	cm s^{-1}	$l\, t^{-1}$
Acceleration (velocity/time)	cm s^{-2}	$l\, t^{-2}$
Force (mass × acceleration)	dyne	$m\, l\, t^{-2}$
Work, energy (force × distance)	erg	$m\, l^2\, t^{-2}$
Gas constant (energy/mol deg)	erg mol^{-1} degree^{-1}	$m\, l^2\, t^{-2}$ deg.$^{-1}$ mol^{-1}
Faraday (charge mol)	coulomb	$m^{\frac{1}{2}}\, l^{\frac{1}{2}}$ mol^{-1}

As a simple example of analysing the dimensions of the rate constant of a reaction, let us convert the units of the rate constant, k, of the reaction $2A \rightarrow B$.

$$k = 6 \cdot 02 \times 10^7 \text{ litre mol}^{-1} \text{ s}^{-1}$$
$$= \frac{6 \cdot 02 \times 10^7 \text{ litre}}{\text{mol. s.}} \cdot \frac{1000 \text{ cm}^3}{\text{litre}} \cdot \frac{\text{mol}}{6 \cdot 02 \times 10^{23} \text{ molecules}}$$
$$= 1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$$
$$= 1 \times 10^{-13}\, l^3\, t^{-1} \quad \text{molecule}^{-1}$$

In chemistry, we encounter energy in various modes; expansion of a gas (*PV* work in units of litre atmospheres), heat (calories per mole), or electrical work (volt coulombs). In all these cases, the ultimate dimensions of the energy will be ml^2t^{-2}. For example, the units of pressure (force/area), can be analysed as $mlt^{-2}\,.l^{-2} = ml^{-1}\,t^{-2}$, and of volume, l^3. Hence energy is also expressible as $(PV) = ml^2t^{-2}$. Since energy is expressed in various common units depending on the situation, it should be possible to arrive at conversion factors between the various units of the same quantity. These conversions are given on the inside cover of the book.

Answers to Select Problems

2. 1 Mass of a single atom:
$S = 5.33 \times 10^{-22} g$; $Xe = 21.8 \times 10^{-23} g$;
$U = 39.6 \times 10^{-23}$ g
Number of atoms in 0·1 g: $s = 18.75$
$\times 10^{21}$; $xe = 4.58 \times 10^{21}$; $u = 2.53$
$\times 10^{21}$

2. 3 (a) 0·005 mol; (b) 0·05 mol; (c) 0·04 mol

2. 5 (i) $Al_2C_2O_9$

2. 6 1568 litre

2. 7 $Pt\,Cl_2$

2. 9 6·72 litre

2.11 3·20 g

3. 1 1.1×10^{27}

3. 2 5.46×10^{-4} g

3. 4 (a) 2×10^{-5}; (b) 8×10^{-16}

3. 6 (a) 3.05×10^5 coulomb/cc; (b) 3·8 $\times 10^{20}$ coulomb/cc

3. 8 (a) 0·529 A; (b) 2.185×10^8 cm s^{-1}; (c) 2.175×10^{-11} erg; (d) -4.348×10^{-11} erg; (e) 1.99×10^{-19} g cm s^{-1}; (f) 1.054×10^{-27} erg s; (g) 2.175×10^{-11} erg

3.10 (a) 15, 240 cm^{-1}

3.11 (b) 6.6×10^{-27} g cm s^{-1}

4. 4 (a) F_2^+; (e) Be_2^+

4. 8 sp^2

4.16 12·48D; 80·13%

4.17 Square planar only

4.22 (a) 50 g cm²; (b) 14.48×10^{-40} g cm²

4.24 1·29 A

4.25 2400 cm^{-1}

6.16 3.22×10^7 molecules

6.17 0·75 mol; 4.52×10^{23} molecules; 18.1×10^{23} atoms

6.18 56 g mol^{-1}

6.20 0·571 atm

6.21 1·48 cm

6.23 (a) 28·98 g mol^{-1}; (b) O_2, 24·5%; N_2, 75·5%

6.27 35·76 g mol^{-1}

6.29 $^{235}UF_6$: $^{238}UF_6 = 1.004 : 1.000$

6.32 5.0×10^{-13} erg molecule^{-1}; 2421 K

6.34 600 K

6.36 1.04×10^5 K

6.40 40 g mol^{-1}

7. 1 263·9 kcal mol^{-1}

7. 4 AB_3

7. 5 5·64 A

7. 7 2·93 A

7. 8 BCC; 8·071 g/cc
FCC; 8·570 g/cc

7.12 6

7.14 85% in both cases

8. 9 361·3 K

8.10 1·269 g

8.12 0·043 atm

8.13 2·232 cm

8.14 0·183 cm

8.15 203·8 cm

8.16 1·755 centipoise

8.17 24·84 millipoise

9. 2 $w = 480$ cal; $q = 480$ cal; $\Delta E = 0$

9. 3 $w = 605$ cal; $q = -36.5$ kcal; $\Delta E = -37.105$ kcal

9. 7 86 kcal

9. 8 218·2 kcal

9. 9 (a) 24·7 kcal; (b) 2·1 kcal

9.11 $\Delta S_{stone} = 0$; $\Delta S_{lake} = 0.777$ cal deg^{-1}; $\Delta S_{universe} = 0.777$ cal deg^{-1}
For reversible lowering: $\Delta S_{stone} = 0$; $\Delta S_{lake} = 0$; $\Delta S_{universe} = 0$
Loss in available energy = 233·1 cal

9.13 (a) 0·886 cal deg^{-1}; (b) 7·85 cal deg^{-1}

9.14 -29.95 kcal

9.16 4·49 kcal

10. 2 (a) 3; (b) 2 and 2; (c) 1; (d) 10; (e) 1

10. 6 77·9° C

10. 7 81·76° C and 65·51° C

10. 9 81·9° C

10.10 0·489 atm

10.13 N_2O_4 2·492 mol litre^{-1};
  NO_2 0·0156 mol litre^{-1}

10.14 0·0581

10.15 0·59 atm

11. 3 (a) (i) $H_2PO_4^-$ (ii) HPO_4^{2-} (iii) NH_2^- (iv) S^{2-} (v) H_2O (vi) OCl^- (vii) $Al(H_2O)_5 (OH)^{2+}$ (viii) CH_3O^- (ix) phenolate anion $C_6H_5O^-$ (x) O^{2-}
  (b) (i) HF (ii) H_2O (iii) HPO_4^{2-} (iv) NH_4^+ (v) NH_3 (vi) H_2S (vii) HSO_4^- (viii) $CH_2OH_2^+$ (ix) H_2CO_3 (x) $C_6H_5NH_3^+$

11.10 (a) $2·0 \times 10^{-5}$ (b) 6·20 (c) $3·98 \times 10^{-4}$ (d) 12·7 (e) $7·94 \times 10^{-12}$ (f) 2·30 (g) 1·0 (h) $1·0 \times 10^{-1}$ (i) $8·0 \times 10^{-4}$ (j) $[OH^-] = 7·76 \times 10^{-10}$; $pH = 4·89$; $pOH = 9·11$

11.11 Ionisation constant $= 1·8 \times 10^{-16}$; Ionic product $= 1·0 \times 10^{-14}$

11.13 (a) Degree of dissociation $= 8·48 \times 10^{-3}$; $[H^+] = 2·12 \times 10^{-3} M$
  (b) Degree of dissociation $= 7·2 \times 10^{-5}$; $[H^+] = 1·80 \times 10^{-5} M$

11.14 $pH = 4·83$

11.15 $[OH^-] = 9·0 \times 10^{-6} M$

11.20 $[H^+] = [SH^-] = 10^{-4} M$; $[S^{2-}] = 10^{-10} M$; and $[H_2S] = 10^{-1} M$

11.23 0·103 g

11.26 Lewis acid, base, acid, acid, base, acid, acid, base, acid, and base respectively

11.27 Li^+ acid: water base; Li^+ acid: $HCONH_2$ base; benzene acid: I_2 base; H_2O acid: H_2O base; and R_2COH^+ acid: HSO_4^- base

12. 2 $2·0 \times 10^{-8}$

12. 3 $5·75 \times 10^4$ litre

12. 4 $4·996 \times 10^5$ s; 0·3177 g

12. 5 $2·8 \times 10^5$ amperes per day

12.10 (a) 3·73 V; (b) 1·234 V

12.11 -2; $+4$; $+6$; $+4$; $+7$

12.12 -1; $+1$; $+5$; $+7$; $+4$

12.13 $+1(N_2O)$; $+2(NO)$; $+3(N_2O_3)$; $+4(NO_2)$; $+5(N_2O_5)$

13. 1 4·43 mm; 0·03 mol litre s^{-1}

13. 2 4×10^{-4} mol litre^{-1} s^{-1}

13. 3 First order; $5·23 \times 10^{-2}$ hr^{-1}; $t_{1/2} = 13·25$ hr

13. 5 10·1 kcal

13. 7 1×10^9 atoms

13. 9 (a) 22·2 kcal; (b) 23·6 kcal

13.12 Acid hydrogen

13.13 9900 years

Index

CONVERSION FACTORS

One erg
$= 10^{-7}$ joule
$= 2 \cdot 389 \times 10^{-8}$ cal
$= 6 \cdot 242 \times 10^{11}$ ev
$= 1 \cdot 113 \times 10^{-24}$ kg*
$= 670 \cdot 5$ amu

One calorie (cal)
$= 4 \cdot 1840 \times 10^7$ erg
$= 4 \cdot 187$ joule
$= 2 \cdot 613 \times 10^{19}$ ev
$= 4 \cdot 659 \times 10^{-17}$ kg
$= 2 \cdot 807 \times 10^{-10}$ amu

One electron volt (ev)
$= 1 \cdot 602 \times 10^{-12}$ erg
$= 1 \cdot 602 \times 10^{-19}$ joule
$= 3 \cdot 827 \times 10^{-20}$ cal
$= 1 \cdot 783 \times 10^{-36}$ kg
$= 1 \cdot 074 \times 10^{-19}$ amu

One kilogram (kg)
$= 8 \cdot 987 \times 10^{23}$ erg
$= 8 \cdot 987 \times 10^{16}$ joule
$= 2 \cdot 142 \times 10^{16}$ cal
$= 5 \cdot 610 \times 10^{35}$ ev
$= 6 \cdot 025 \times 10^{26}$ amu

One atomic mass unit (amu)
$= 1 \cdot 492 \times 10^{-3}$ erg
$= 1 \cdot 492 \times 10^{-10}$ joule
$= 3 \cdot 564 \times 10^{-11}$ cal
$= 9 \cdot 310 \times 10^8$ ev
$= 1 \cdot 660 \times 10^{-27}$ kg

*Mass units are included as energy equivalents.

FUNDAMENTAL CONSTANTS

Avogadro number	N_0	$6 \cdot 0225 \times 10^{23}$ molecules mol^{-1}
Boltzmann constant	k	$1 \cdot 3805 \times 10^{-16}$ erg K^{-1} molecule^{-1}
Charge on the electron	e	$4 \cdot 8030 \times 10^{-10}$ esu
		$1 \cdot 6021 \times 10^{-19}$ coulomb
Electron rest mass	m	$9 \cdot 1091 \times 10^{-28}$ g
		$0 \cdot 00055$ amu
Neutron rest mass	M_n	$1 \cdot 6749 \times 10^{-24}$ g
		$1 \cdot 008665$ amu
Proton rest mass	M_p	$1 \cdot 6725 \times 10^{-24}$ g
		$1 \cdot 007277$ amu
Planck's constant	h	$6 \cdot 6256 \times 10^{-27}$ erg s
Gas constant	R	$0 \cdot 820541$ atm K^{-1} mol^{-1}
		$8 \cdot 3143$ joule K^{-1} mol^{-1}
		$1 \cdot 9872$ cal K^{-1} mol^{-1}
Faraday's constant	F	$9 \cdot 6487 \times 10^4$ coulomb equivalent^{-1}
Speed of light	c	$2 \cdot 997925 \times 10^{10}$ cm s^{-1}

Unlike traditional undergraduate chemistry textbooks, this book provides a common platform for an integrated approach into the principles and practice of chemistry and chemical science. More emphasis is thus placed not only on the interplay amongst the various traditional divisions of chemistry, such as organic, inorganic, physical and so on but also on the interfaces which chemistry today shares with other sciences. The text is therefore useful not only to students of pure and applied sciences but also to scholars of engineering, medicine agriculture.

The content of the book is arranged under the broad divisions of structure, energy and transformations. The book opens with a discussion on the nature and scope of chemical science. Chapters 2 to 8 cover structure and properties of systems, Chapters 9 to 12 are on thermodynamics and equilibria and deal with energy, and Chapters 13 to 17 are devoted to transformation in inorganic and organic systems, although they do include a few structural aspects. Chapter 18 comprehensively combines biological, medical and chemical sciences through the discussion of the living cell, and chapter 19 introduces nuclear chemistry. All through, the emphasis has thus been on the chemist's microscopic approach.

Innumerable examples drawn from inorganic, organic and biological systems admirably illustrate the wide variety of applications of chemical principles. Wherever possible, the text has been saved from exhaustive mathematical treatment. This will not impede the comprehension of the text by students lacking in mathematical background.

Professor C N R Rao is presently the Director of the Indian Institute of Science, Bangalore.

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